INTERNATIONAL PATENT OFFICE

WORLD ORGANIZATION FOR INTELLECTUAL PROPERT

International Bureau

International application published on the basis of the Paten;

Cooperation Treaty (PCT)

International Patent No. WO 00/24685 A1

Int. Cl.⁷:	C03C	3/06
	C03B	8/04
		20/00
	G03F	1/16
	G02B	1/00
	H01L	21/027

Int. Cl.^{7}:
C03C 3/06
C03B 8/04
    20/00
G03F 1/16
G02B 1/00
H01L 21/027

Int. Filing No.:   PCT/JP99/05995

Int. Filing Date: October 28, 1999

Int. Publication Date: May 4, 2000

Priority
>   Date: October 28, 1998
>   Country: JP
>   No.:   Hei 10[1998]-307476
>
>   Date: November 30, 1998
>   Country: JP
>   No.:   Hei 10[1998]-338636
>
>   Date: December 9, 1998
>   Country: JP
>   No.:   Hei 10[1998]-350116
>
>   Date: December 11, 1998
>   Country: JP
>   No.:   Hei 10[1998]-353339
>
>   Date: December 11, 1998
>   Country: JP
>   No.:   Hei 10[1998]-353351

Date:	December 24, 1998
Country:	JP
No.:	Hei 10[1998]-367671

Date:	December 25, 1998
Country:	JP
No.:	Hei 10[1998]-370014

Date:	March 31, 1991
Country:	JP
No.:	Hei 11[1999]-93613

Date:	September 28, 1999
Country:	JP
No.:	Hei 11[1999]-275030

SYNTHETIC QUARTZ GLASS AND METHOD FOR PRODUCTION THEREOF

Inventors:

Yoshiaki Ikuta
Shinya Kikugawa
Noriaki Shimodaira
Akio Masui
Asahi Glass Co., Ltd.
1150 Hazawa-cho, Kanagawa-ku,
Yokohama-shi, Kanagawa-ken
Japan 221-8755

Shuhei Yoshizawa
Asahi Glass Co., Ltd.
2-1-2 Marunouchi, Chiyoda-ku,
Tokyo, Japan 100-8305

Applicant:

Asahi Glass Co., Ltd.
1-12-1 Yuraku-cho, Chiyoda-ku,
Tokyo

Agents:

Toshiharu Ogawa et al., patent
attorney

Designated States:

US, European Patent, (AT, BE, CH,
CY, DE, DK, ES, FI, FR, GB, GR,
IE, IT, LU, MC, NL, PT, SE)

(57) Abstract

A synthetic quartz glass for optical use which is used through irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, characterized in that the quartz glass contains fluorine and has a ratio of the intensity of a scattering peak at 2250 cm^{-1} (I_{2250}) to that of a scattering peak at 800 cm^{-1} (I_{800}), that is I_{2250}/I_{800}, in a laser Raman spectrum of 1×10^{-4} or less and an absorption coefficient of the light having a wave length of 245 nm of 2×10^{-3} cm^{-1} or less.

FOR INFORMATION ONLY

Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT.

AL	Albania	KZ	Kazakhstan
AM	Armenia	LC	Saint Lucia
AT	Austria	LI	Liechtenstein
AU	Australia	LK	Sri Lanka
AZ	Azerbaijan	LR	Liberia
BA	Bosnia-Herzegovina	LS	Lesotho
		LT	Lithuania
BB	Barbados	LU	Luxembourg
BE	Belgium	LV	Latvia
BF	Burkina Faso	MC	Monaco
BG	Bulgaria	MD	Republic of Moldavia
BJ	Benin		
BR	Brazil	MG	Madagascar
BU	Bulgaria	MK	Macedonia (former Republic of Yugoslavia)
BY	Belarus		
CA	Canada		
CF	Central African Republic	ML	Mali
		MN	Mongolia
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CI	Côte d'Ivoire	MX	Mexico
CM	Cameroon	NE	Niger
CN	China	NL	Netherlands
CU	Cuba	NO	Norway
CY	Cypress	NZ	New Zealand
CZ	Czech Republic	PL	Poland
DE	Germany	PT	Portugal
DK	Denmark	RO	Romania
EE	Estonia	RU	Russian Federation
ES	Spain		
FI	Finland	SD	Sudan
FR	France	SE	Sweden
GA	Gabon	SG	Singapore
GB	United Kingdom	SI	Slovenia
GE	Georgia	SK	Slovak Republic
GH	Ghana	SL	Sierra Leone
GM	Gambia	SN	Senegal
GN	Guinea	SZ	Swaziland
GR	Greece	TD	Chad
GW	Guinea-Bissau	TG	Togo
HR	Croatia	TJ	Tajikstan
HU	Hungary	TM	Turkmenistan
ID	Indonesia	TR	Turkey
IE	Ireland	TT	Trinidad and Tobago
IL	Israel	UA	Ukraine
IS	Iceland	UG	Uganda
IT	Italy	US	United States of America
JP	Japan	UZ	Uzbekistan
KE	Kenya	VN	Vietnam
KG	Kyrgyzstan	YU	Yugoslavia
KP	Democratic People's Republic of Korea	ZA	South Africa
		ZW	Zimbabwe
KR	Republic of Korea		

. The present invention relates to a synthetic quartz glass to be used for optical parts of devices utilizing ultraviolet rays with a wavelength of 400 nm or less as a light source and its production method. More specifically, it relates to a synthetic quartz glass to be used for optical parts (include manufactured articles and semi-manufactured articles) such as lenses (for a projection system, illumination system), prisms, etalons, photomasks, pericles (pericle material, pericle frame, or both), window materials, which are used for light from the ultraviolet region to the vacuum ultraviolet region emitted from excimer lasers (XeCl: 308 nm, KrF: 248 nm, ArF: 193 nm), F_2 laser (157 nm), low pressure lamp (185 nm), Xe_2^* excimer lamp (172 nm), deuterium lamp (110-400 nm), etc., and production methods thereof.

Background of the invention

Synthetic quartz glass has special features such that it is a material transparent over a wide wavelength region from the near infrared to the vacuum ultraviolet, and it has an extremely low thermal expansion coefficient and excellent dimensional stability, and further it contains almost no impurities and has high purity. Thus, synthetic quartz glass has been used mainly for optical components of optical devices utilizing a conventional g line (436 nm) and i line (365 nm) light source.

In recent years, technology for drawing fine patterns with finer line width in photolithography for drawing integrated circuit patterns on wafers has been demanded in conjunction with high integration of LSI, and as a countermeasure a trend in the exposure light source toward a shorter wavelength has been promoted. For instance, KrF excimer lasers, ArF excimer lasers, and furthermore F_2 lasers, instead of conventional g line and i line sources, have been used as light sources of steppers for lithography.
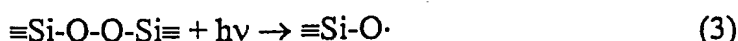
In addition, low pressure mercury lamps, Xe_2^* excimer lamps, or deuterium lamps are used in (1) devices such as an optical CVD, (2) an ashing device or etching device for silicon wafers, or (3) ozone generators, etc., and in addition, development for application to photolithography has been promoted. It is necessary to use synthetic quartz glass for gas enclosed tubes used in low pressure mercury lamps, excimer lamps, deuterium lamps, etc., and for optical components utilizing short-wavelength light such as the aforementioned optical devices utilizing short-wavelength light sources.

A synthetic quartz glass to be used for the aforementioned optical components should exhibit transmittance of light from the ultraviolet region to the vacuum ultraviolet region and the transmittance should not be lowered by ultraviolet ray irradiation (hereinafter, simply called "UV resistance"). In addition, optical components which are used by irradiating with light from sources such as ArF excimers, F_2 lasers, low pressure mercury lamps, Xe_2^* excimer lamps, etc., should exhibit excellent light transmittance in the vacuum ultraviolet region at a wavelength of

200 nm or less (hereinafter simply called "vacuum UV transmittance"). Further, for optical components which are used for light at a wavelength of 200 nm or less, the refractive index fluctuation width (Δn) should be smaller than for conventional ones (hereinafter called "homogeneity").

When conventional synthetic quartz glass is irradiated with high energy light emitted from a light source such as a KrF excimer laser, ArF excimer, etc., new absorption bands are formed in the ultraviolet region, and this causes a problem in optical components in an optical system utilizing ultraviolet rays as a light source. Namely, if it is irradiated with ultraviolet rays for a long time, an absorption band at about 215 nm, so-called E' centers ($\equiv$Si·), and an absorption band at about 260 nm, so-called NBOHC's (non-crosslinking oxygen radical: $\equiv$Si-O·), are formed.

The cause for the formation of those absorption bands can be classified into two parts. One is structural defects of the synthetic quartz glass, namely, reduction defects such as $\equiv$Si-Si$\equiv$ (oxygen deficient defect) and $\equiv$Si-H, etc., or oxidation defects such as $\equiv$Si-O-O-Si$\equiv$, etc. while the other is the unstable structure of synthetic quartz glass, namely due to three-member ring structures or four-member ring structures. It is thought that if those defects are cleaved by irradiation of ultraviolet rays as shown in the equations (1)-(4) below to form paramagnetic defects (E' centers and NBOHC's) those cause the reduction of transmittance, the reduction of UV resistance, increase of absolute refractive index, fluctuation of refractive index distribution, and/or fluorescence.

$$\equiv\text{Si-Si}\equiv + h\nu \rightarrow 2\equiv\text{Si}\cdot \qquad (1)$$
$$\equiv\text{Si-H} + h\nu \rightarrow \equiv\text{Si}\cdot + \text{H}\cdot \qquad (2)$$
$$\equiv\text{Si-O-O-Si}\equiv + h\nu \rightarrow \equiv\text{Si-O}\cdot \qquad (3)$$
$$\equiv\text{Si-O-Si}\equiv + h\nu \rightarrow \text{Si}\cdot + \equiv\text{Si-O}\cdot \qquad (4)$$

Various methods have been investigated for solving the aforementioned problems, and it is known that it is allieviated if hydrogen molecules of a certain form are included in the synthetic quartz glass. For instance, a method of suppressing the reduction of transmittance which is caused by irradiation of ultraviolet rays, by including hydrogen molecules at 5×10^{16} molecules/cm^3 or higher and also OH groups at 100 ppm or higher in a synthetic quartz glass is disclosed in Japanese Kokai Patent Application No. Hei 3[1991]-88742.

However, OH groups of a synthetic quartz glass react by irradiation with ultraviolet rays according to the following equation (5) to form NBOHC's to produce 260 nm absorption and 650 nm fluorescence, which are problems.

$$\equiv\text{Si-OH} + h\nu \rightarrow \equiv\text{Si-O}\cdot \text{(NBOHC)} + \text{H}\cdot \qquad (5)$$

Even when hydrogen molecules are included, the reaction of equation (5) cannot be completely prevented, and especially when the concentration of OH groups is high, the 650 nm

fluorescence intensifies and causes problems. In addition, if the concentration of OH groups is high the transmittance of light at 150-180 nm decreases, and this causes a problem especially in those devices utilizing low pressure mercury lamp, Xe_2^* excimer lamp, F_2 laser, etc. as a light source.

To solve those problems, a synthetic quartz glass having an OH group concentration of 10 ppm or less and also a halogen concentration of 400 ppm or higher and containing hydrogen molecules is proposed in Japanese Kokai Patent Application No. Hei 6[1994]-227827. This glass has excellent UV resistance since the OH group concentration is low and high transmittance at 150-180 nm is obtained.

In Japanese Kokai Patent Application No. Hei 6[1994]-227827, a method for manufacture of a synthetic quartz glass was proposed, which is characterized by comprising (1) a process of forming a porous quartz glass body by flame hydrolysis of a glass forming raw material, (2) a process of dehydrating the porous quartz glass body by heating in a halogen-containing atmosphere at 800-1250°C, (3) a process of vitrifying the dehydrated porous quartz glass body by heating to a temperature that makes the porous quartz glass transparent and vitrifying, and (4) a process of heating the resulting transparent synthetic quartz glass in a hydrogen-containing atmosphere at 500-1100°C to include hydrogen in the synthetic quartz glass.

Furthermore, since the reduction defects of ≡Si-Si≡ and ≡Si-H easily form if a synthetic quartz glass is held in a hydrogen-containing environment at high temperature, a method for producing a synthetic quartz glass by forming a fluorine-containing quartz glass in almost the same manner as in Japanese Kokai Patent Application No. Hei 6[1994]-227827 and heating it in a hydrogen-containing atmosphere at 500°C or less to include hydrogen is disclosed in Japanese Kokai Patent Application Hei 8[1996]-75901.

However, the present inventors examined the methods described in Japanese Kokai Patent Application No. Hei 6[1994]-227827 and Japanese Kokai Patent Application No. Hei 8[1996]-75901 to confirm that sufficient UV resistance cannot always be obtained. Namely, if a porous quartz glass body is treated in a fluorine compound-containing environment at a high temperature of 800-1250°C, the aforementioned ≡Si-Si≡ defects form. This ≡Si-Si≡ defect causes a problem since as explained above E' centers are formed by irradiation with ultraviolet rays and also absorption occurs at 245 nm and 163 nm.

In addition, the ≡Si-Si≡ defect produces ≡Si-H by equation (6) shown below when it [the quartz] is treated in a hydrogen-containing environment, and this ≡Si-H also produces E' centers, which is also a problem.

$$\equiv Si\text{-}Si \equiv + H_2 \rightarrow \equiv Si\text{-}H + \equiv Si\text{-}H \qquad (6)$$
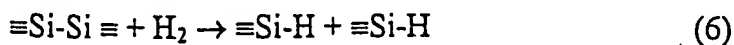
On the other hand, to improve vacuum ultraviolet ray transmittance, a synthetic quartz glass with an OH group concentration of 200 ppm or less, a chlorine concentration of 2 ppm or

less, and a ≡Si-Si≡ concentration of 1 x 10^{15}/cm^3 or less was proposed in Japanese Kokai Patent Application No. 8[1996]-91867 Further, a synthetic quartz glass with an OH group concentration of 10-400 ppm and also a reduction defect concentration and an oxidation defect concentrations of at most 5 x 10^{16}/cm^3 each was proposed in Japanese Kokai Patent Application No. Hei 9[1997]-235134. A synthetic quartz glass having an OH group concentration of 100-2,000 ppm and also containing transition metals, alkali metals, or alkaline earth metals at amounts less than prescribed concentrations, respectively, is proposed in Japanese Kokai Patent Application No. Hei 7[1995]-267674

In all of those conventional synthetic glasses, it was planned to improve the vacuum ultraviolet ray transmittance by controlling the OH group concentration in a prescribed range, but high transmittance in the vacuum ultraviolet region was not always obtained.

In addition, as a method for securing the homogeneity of synthetic quartz glass, a method of including both the OH groups and chlorine in the synthetic quartz glass to control the fluctuation width of the OH group and chlorine concentration was disclosed in Japanese Kokoku Patent No. Hei 6[1994]-27014. However, the chlorine exists in the form of ≡Si-Cl in the synthetic quartz glass and the bonding energy of this ≡Si-Cl is weak, 7-8 eV, so that it is easily cleaved by irradiation with ultraviolet rays as shown in the following equation to also produce E' centers.

≡Si-Cl + hν → ≡Si· (E' center) + Cl·
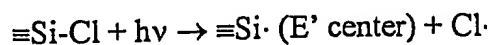
Thus, in the method described in the aforementioned patent, there is a problem in UV resistance although a synthetic quartz glass having excellent homogeneity is obtained.

The present invention provides a synthetic quartz glass wherein the production of E' centers and fluorescence radiation is reduced and the UV resistance is excellent.

The present invention further provides a synthetic quartz glass that is excellent with regard to vacuum ultraviolet ray transmittance.

The present invention provides a synthetic quartz glass that is excellent with regard to homogeneity.

The present invention provides a preferable method for the production of those synthetic quartz glasses.

Summary of the invention

The present inventors conducted detailed studies on the effect of halogen concentration and stable structure in a synthetic quartz glass on UV resistance and ultraviolet ray transmittance. As a result, it was found that fluorine exists as a form of ≡Si-F, and the bonding energy of this ≡Si-F bond is extremely strong, at least 20 eV, and thus it does not cleave even by irradiation with ultraviolet rays so that there is no problem in UV resistance. It was further found that

fluorine reduces distorted structure in the quartz glass and improves the UV resistance although the mechanism is not established yet.

Thus, the present invention provides a synthetic quartz glass containing fluorine and having a ratio of the intensity of the scattering peak at 2250 cm^{-1} (I_{2250}) to that of the scattering peak at 800 cm^{-1} (I_{800}), that is I_{2250}/I_{800}, in a laser Raman spectrum of 1 x 10^{-4} or less and an absorption coefficient of light with a wavelength of 245 nm (hereinafter simply called 245 nm absorption coefficient) of 2 x 10^{-3} cm^{-1} or less.

Detailed description of the preferred embodiments

The scattering peak at 800 cm^{-1} shows the bond of $\equiv$Si-O- (fundamental vibration between silicon and oxygen), and the scattering peak at 2250 cm^{-1} shows the bond of $\equiv$Si-H, which is a reduction defect, further the I_{2250}/I_{800} ratio becomes an index for the concentration ($\equiv$Si-H concentration) of the $\equiv$Si-H defect. In the present invention, it is important that the I_{2250}/I_{800} ratio be 1 x 10^{-4} or less. If it exceeds 1 x 10^{-4}, E' centers easily form.

The 245 nm absorption coefficient becomes an index for the concentration of the $\equiv$Si-Si$\equiv$ defect which is also a reduction defect. In the present invention, it is important that the 245 nm absorption coefficient be 2 x 10^{-3} cm^{-1} or less. If it exceeds 2 x 10^{-3} cm^{-1}, E' centers also easily form. In addition, if it exceeds 2 x 10^{-3} cm^{-1}, it is difficult to attain high transmittance at 150-180 nm. Further, it is preferred to reduce the absorption of light at 163 nm.

In the present invention, the stipulation of a scattering peak at 2250 cm^{-1} and the stipulation of a 245 nm absorption coefficient prescribe the amount of reduction defects.

The concentration of E' centers can be evaluated by measuring the transmittance of light at 214 nm immediately after shot irradiation of a KrF excimer laser beam using an ultraviolet visible spectrophotometer and determining the change ΔK_{214} [cm^{-1}] of the absorption coefficient before and after irradiation. It is preferred that ΔK_{214} be 1 x 10^{-1} or less. Especially, a ΔK_{214} of 1 x 10^{-2} or less is preferred.

The extent of fluorescence illumination can be evaluated by measuring the 650 nm fluorescence intensity L_{650} and KrF excimer laser scattering light intensity S_{248} from the direction perpendicular to the incidence axis of a KrF excimer laser beam when a KrF excimer laser beam is shot irradiated and determining the ratio L_{650}/S_{248} of the 650 nm fluorescence intensity to the KrF excimer laser (248 nm) scattering light intensity. It is preferred that L_{650}/S_{248} be 5 x 10^{-4} or less and more preferably 1 x 10^{-4} or less.

In addition, the present inventors investigated the effect of halogen concentration and OH group concentration in a synthetic quartz glass on UV resistance and found that the action of fluorine is different from that of chlorine in the synthetic quartz glass. The chlorine exists as a form of $\equiv$Si-Cl in the synthetic quartz glass, and since the $\equiv$Si-Cl bond has a weak bonding

energy of 7-8 eV and it is easily cleaved by ultraviolet ray irradiation according to the following equation to form the aforementioned E' centers,

$$\equiv Si\text{-}Cl + h\nu \rightarrow \equiv Si\cdot \text{ (E' center)} + Cl\cdot \quad\quad (7)$$
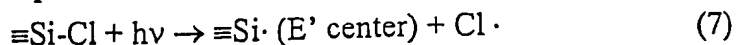
it lowers the UV resistance.

Furthermore, a synthetic quartz glass containing no chlorine, prepared using glass raw materials containing no chlorine, was also proposed (Japanese Kokai Patent Application No. Hei 7[1995]-291635). It has a fluorine concentration of at least 1,000 ppm for inhibiting the reduction of transmittance by irradiation of high energy light and an OH group concentration of at least 50 ppm for inhibiting the absorption at 245 nm by the oxygen-deficiency defect $\equiv Si\text{-}Si\equiv$, but the problem of the reduction of transmittance at 150-180 nm was not mentioned at all so there was a difficulty when it was used for devices utilizing low pressure mercury lamp, Xe_2^* excimer lamp, F_2 laser, etc., as a light source.

Thus, it was thought that it is necessary for inhibiting the formation of paramagnetic defects and improving the essential UV resistance to optimize the OH group, chlorine, and fluorine concentrations and further investigations of this were conducted to determine that if the fluorine concentration in a synthetic quartz glass is increased and the chlorine concentration is decreased, a synthetic quartz glass having excellent UV resistance can be obtained when the OH group concentration is slightly lowered.

Namely, the present invention provides a synthetic quartz glass containing fluorine for decreasing the content of reduction defects below a specified quantity and having a chlorine concentration of 100 ppm or less. Especially, as a synthetic quartz glass having excellent UV resistance and effective for inhibiting the formation of an unstable structure, E' centers, and fluorescence illumination, characterized by having an OH group concentration of less than 50 ppm, a fluorine concentration of 100 ppm or higher, a chlorine concentration of 100 ppm or less, and a hydrogen molecule concentration of 5×10^{16} molecules/cm^3 or higher, is preferred.

In addition, the mutual relation between the effect of the halogen concentration and the hydrogen molecule concentration of a synthetic quartz glass and the effect of unstable structure in the synthetic quartz glass was investigated. As a result, it was found that if the existing amount of unstable structure by fluorine doping is reduced to a fixed limit, and at the same time action for removing paramagnetic defects with hydrogen molecules is employed, the ultraviolet ray transmittance and the UV resistance of a synthetic quartz glass to light emitted from a short-wavelength light source can be improved to a satisfactory level.

With this, it was found that among synthetic quartz glasses of the present invention, a synthetic quartz glass having a ratio, I_1/I_0, of the intensity of the scattering peak at 495 cm^{-1} (I_1) in a laser Raman spectrum from the unstable structure in the synthetic quartz glass to that of the scattering peak at 440 cm^{-1} (I_0) and a ratio, I_2/I_0, of the intensity of the scattering peak at 606 cm^{-1}

(I_2) to I_0 that are both in a specified range is effective for improvement of the ultraviolet ray transmittance and the UV resistance.

Based on this finding, the present invention provides a synthetic quartz glass, characterized in that the quartz glass contains fluorine to decrease reduction defects below a specified quantity and has a ratio of the intensity of the scattering peak at 495 cm^{-1} (I_1) in a laser Raman spectrum to that of the scattering peak at 440 cm^{-1} (I_0), that is I_1/I_0, of ≤ 0.585 and a ratio of the intensity of the scattering peak at 606 cm^{-1} (I_2) to I_0, that is I_2/I_0, of ≤ 0.136. Especially, it is preferred to contain fluorine at 100 ppm or higher and hydrogen molecules at 5×10^{16} molecules/cm^3 or higher.

It is preferred for the synthetic quartz glass of the present invention to contain fluorine at 100 ppm or more (here ppm means weight ppm, and hereinafter it is the same, ppb has also the same meaning). If it is less than 100 ppm, sometimes the function of reducing the unstable structure in the synthetic quartz glass is not sufficient. It is further preferred that the fluorine concentration be 400 ppm or higher, and a range of 400-3,000 ppm is particularly preferred. When the fluorine concentration exceeds 3,000 ppm, there is a possibility of producing reduction defects to lower the UV resistance.

It is preferred in the synthetic glass of the present invention that the OH group concentration be 100 ppm or less. If it exceeds 100 ppm, the transmittance in the wavelength region of about 170 nm or less is lowered, and the glass may not be suitable in optical components of devices utilizing, e.g., a Xe$_2$* excimer lamp. F$_2$ laser, and deuterium lamp as a light source. If the OH group concentration is 50 ppm or less, good UV resistance is obtained, and an OH group concentration of 20 ppm or less, furthermore less than 10 ppm, is preferred since high transmittance is obtained in the vacuum ultraviolet region. Especially, the OH group concentration influences the light transmittance in the vacuum ultraviolet region at 200 nm or less, and an OH group concentration of less than 10 ppm is preferred in synthetic quartz glass which is used for light having a wavelength of 175 nm or less in the vacuum ultraviolet region. Furthermore, an OH group concentration of 5 ppm or less is preferred in synthetic quartz glass which is used for light having a wavelength of less than 160 nm or less in the vacuum ultraviolet region.

In addition, the oxygen-deficient defect ($\equiv$Si-Si$\equiv$) largely influences the vacuum ultraviolet ray transmittance, and this oxygen-deficient defect has an absorption band centered at a wavelength of 163 nm. The internal transmittance Γ_{163} (%/cm) at a wavelength of 163 nm is presumed from the OH group concentration C_{OH} (ppm) in a synthetic quartz glass from the following equation (a) [sic; i].

$$T_{163} \text{ (%/cm)} \geq \exp(-0.02C_{OH}^{0.85}) \times 100 \qquad \text{(i)}$$

. However, if oxygen-deficient defects exist, the actual transmittance (T_{163}) at a wavelength of 163 nm becomes smaller than the value of the right side of the equation (i) since there is an absorption band centered at 163 nm, and the transmittance at a wavelength of 200 nm or less decreases in dependence upon the size of the absorption band. Thus, it is important for obtaining excellent vacuum ultraviolet ray transmittance for the glass to contain practically no oxygen-deficient defects, and it is preferred for it to contain practically no oxygen-deficient defects, if the equation (i) relating to the internal transmittance at a wavelength of 163 nm is to be satisfied.

In addition, it is preferred that the synthetic quartz glass of the present invention have an internal transmittance at 157 nm of 70%/cm and especially an internal transmittance of 80%/cm or higher from the viewpoint of vacuum ultraviolet ray transmittance.

In the synthetic quartz of the present invention, the lower the chlorine concentration is, the better, and if the chlorine concentration is 100 ppm or less, satisfactory UV resistance is obtained; further a chlorine concentration of 25 ppm or less is preferred from the viewpoint of homogeneity, and especially a chlorine concentration of 10 ppm or less is preferred for satisfactory vacuum ultraviolet ray transmittance to be obtained. Furthermore, from the point of UV resistance in the vacuum ultraviolet region at a wavelength of 175 nm or less, an extremely low chlorine concentration is preferred, and concretely a chlorine concentration of 100 ppb or less, especially 50 ppb or less, is preferred.

If the hydrogen molecule concentration is 5×10^{16} molecules/cm^3 or higher in the . synthetic quartz glass of the present invention, an action for removing paramagnetic defects caused by ultraviolet ray irradiation is created. It is especially preferred to have a hydrogen molecule concentration of at least 1×10^{17} molecules/cm^3, furthermore 1×10^{17}-5×10^{18} molecules/cm^3, especially 5×10^{17}-5×10^{18} molecules/cm^3.

On the other hand, the Si-O-Si bonding angle in the $\equiv$Si-O-Si$\equiv$ bond in a quartz glass network has a certain distribution. Unstable structure in a synthetic quartz glass means a distorted $\equiv$Si-O-Si$\equiv$ bond. If the unstable structure increases, the vacuum ultraviolet ray transmittance decreases since the unstable structure in a synthetic quartz glass has weaker bonding energy than the normal structure. The unstable structure is dependent upon the virtual temperature of the synthetic quartz glass and it is also influenced by the fluorine concentration in the synthetic quartz glass. Namely, if a synthetic quartz glass is doped with fluorine, the unstable structure can be decreased, and in addition the unstable structure is decreased as the virtual temperature decreases. In specific, if the virtual temperature of a synthetic quartz glass is 1100°C or lower, the unstable structure can be decreased, and excellent vacuum ultraviolet ray transmittance is obtained. In this case, a fluorine concentration of 100 ppm or less is preferred. In the present

invention, the virtual temperature means the virtual temperature determined by the method of A. Agarwal et al. (J. Non-Cryst., 185, 191, 1995).

It is preferred to lower the concentrations of metallic impurities such as alkali metals, alkaline earth metals, and transition metals, etc., in the synthetic quartz glass of the present invention as much as possible since they lower the transmittance in the region from the ultraviolet region to the vacuum ultraviolet region and also cause UV resistance. In specific, a total content of metallic impurities of 100 ppb or less and especially 50 ppb or less is preferred.

In addition, if there is distribution in the OH group concentration and the fluorine concentration in a synthetic quartz glass, the homogeneity is deteriorated since the OH group and fluorine in the quartz glass influence refractive index.

It was thought necessary for suppressing the formation of paramagnetic defects to improve UV resistance and homogeneity to optimize the distribution of the OH group concentration and the fluorine concentration, and an investigation on this was conducted. As a result, it was found that the homogeneity can be improved and the OH group concentration in the light transmitting region, namely light applying region, by controlling the distribution of the fluorine concentration and controlling the fluctuation widths of the fluorine concentration and the OH group concentration to 15 ppm or less, respectively.

In addition, it was also found that the homogeneity can be improved even when the upper limit of the fluctuation width of the fluorine concentration and the OH group concentration is at 25 ppm or less if the OH group and chlorine are distributed in the light passing region in such a pattern to mutually negate the concentration distribution.

Accordingly, the present invention provides a synthetic quartz glass containing OH groups and fluorine for optical use through irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, wherein in the optical application region the fluctuation width of the OH group concentration is 15 ppm or less, and the fluctuation width of the fluorine concentration is 15 ppm or less, and the chlorine concentration is 25 ppm or less.

Furthermore it provides a synthetic quartz glass containing OH groups and fluorine with excellent homogeneity and UV resistance, wherein the OH groups and the fluorine are distributed in the optical application region in such a way as to mutually negate concentration distribution and at the same time the fluctuation width of the OH group is 25 ppm or less, and the fluctuation width of the fluorine concentration is 25 ppm or less, and moreover the chlorine concentration is 25 ppm or less.

In the present invention, a synthetic quartz glass wherein both the fluctuation width of the OH group concentration and the fluctuation width of the fluorine concentration in the optical application region are 15 ppm or less is preferred since excellent homogeneity can be stably exhibited. In addition, when the OH groups and fluorine are distributed in the optical application

region in such a way as to mutually negate concentration distribution, excellent homogeneity can be stably exhibited even in the case of a synthetic quartz glass wherein the fluctuation width of the OH group concentration is 25 ppm or less, and the fluctuation width of the fluorine concentration is 25 ppm or less.

In this, the fluctuation width (Δn) of the refractive index in the plane perpendicular to the incident light is preferably 20×10^{-6} or less, especially 10×10^{-6} or less, furthermore 5×10^{-6} or less, and most preferably 2×10^{-6} or less.

It is especially preferred from the viewpoint of Δn that the sum of the fluctuation width of the fluorine concentration and the fluctuation width of the OH group concentration in the optical application region be 5 ppm or less.

In the present invention, the optical application region means the region from the ultraviolet region to the vacuum ultraviolet region where light is transmitted or reflected in the use of synthetic quartz glass. In addition, to distribute the OH groups and fluorine in such a way as to mutually negate the concentration distribution means a distribution state where the fluctuation of the fluorine concentration and the OH group concentration on an optional plane perpendicular to the incident light are complementary to each other in the light transmitting region. Namely, for instance, in the case where fluorine concentration is increased along the outer side from the center of an optional plane, the OH group concentration has a distribution state of decreasing along the outer side from the center of the plane, or the above have the reverse distribution state. More concretely, the fluorine concentration shows a downward convex graph, which has a minimum value at the center in a plane perpendicular to the incident light, while the OH group concentration shows an upward convex graph, which has a maximum value at the center as shown in the graphs showing fluorine concentration and OH group concentration in Tables 14-17 [sic; 15-19] in synthetic quartz glasses of Examples 82-94 to be described later, and both concentrations have a distribution having a complementary relation or the reverse complementary relation.

In the present invention, as the production method of synthetic quartz glass, the direct method, soot method (VAD method, OVD method), plasma methods, etc., can be exemplified. Particularly, the soot method is preferred from the viewpoints that the production temperature is low and the contamination of impurities such as chlorine and metals can be avoided. Further, in the soot method, OH groups are replaced with fluorine by doping with fluorine. According to the soot method, a synthetic quartz glass having a low OH group concentration and excellent ultraviolet ray transmittance can be obtained at high productivity since the doping amount of fluorine is almost equal to the amount of substituted OH groups and the OH groups can be effectively reduced.

.The production of a synthetic quartz glass of the present invention by the soot method will now be explained in detail.

The production of a synthetic quartz glass by the soot method comprises the following (a), (b), and (c) processes.
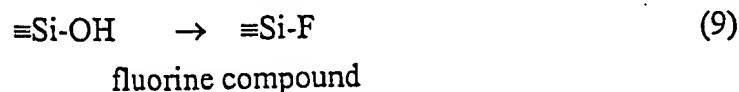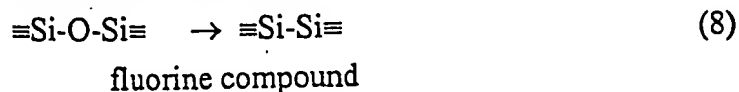
(a) A process of depositing and growing quartz glass fine particles obtained by flame hydrolysis of a quartz glass forming raw material on a substrate to form a porous quartz glass body.

(b) A process of keeping the porous quartz glass body in a fluorine-containing environment to obtain a porous quartz glass body containing fluorine.

(c) A process of heating the fluorine-containing porous quartz glass body to a transparency-forming, vitrifying temperature to obtain a fluorine-containing transparent quartz glass body.

A synthetic quartz glass containing hydrogen is produced according to the following (a), (b'), (c'), and (d) processes by executing those processes in that order.

(a) A process of depositing and growing quartz glass fine particles obtained by flame hydrolysis of a quartz glass forming raw material on a substrate to form a porous quartz glass body.

(b') A process of keeping the porous quartz glass body in a fluorine-containing environment at a temperature of 600°C or lower to obtain a fluorine-containing porous quartz glass body.

(c') A process of heating the fluorine-containing porous quartz glass body in an environment containing practically no fluorine to a transparency-forming, vitrifying temperature to obtain a fluorine-containing transparent quartz glass body.

(d) A process of keeping the fluorine-containing transparent quartz glass in a hydrogen-containing environment at a temperature of 600°C or lower to obtain a synthetic quartz glass containing fluorine and hydrogen.

When the porous quartz glass body is kept in a fluorine compound-containing environment and the temperature is high, $\equiv$Si-Si$\equiv$ defects easily form. Namely, if a porous quartz glass body is treated in a fluorine compound-containing atmosphere at high temperature, the activity of the fluorine compound is strong and thus there is a tendency to form $\equiv$Si-Si$\equiv$ defects by the following equations (8) and (9).

$$\equiv\text{Si-O-Si}\equiv \quad \rightarrow \quad \equiv\text{Si-Si}\equiv \qquad\qquad (8)$$
fluorine compound

$$\equiv\text{Si-OH} \quad \rightarrow \quad \equiv\text{Si-F} \qquad\qquad (9)$$
fluorine compound

If a porous quartz glass body is treated in a fluorine compound-containing atmosphere at a low temperature such as 600°C or lower, the activity of the fluorine compound can be suppressed and only the reaction of equation (9) advances without progress in the reaction of equation (8) and thus $\equiv$Si-Si$\equiv$ defects do not form.

Next, each process will be explained. In process (a), a quartz glass forming raw material, oxygen gas, and hydrogen gas are fed to a multichannel burner and flame hydrolyzed to obtain quartz glass fine particles, and those particles are deposited and grown on a substrate to form a porous quartz glass body. The quartz glass forming raw material is not particularly restricted as long as it is a gas-forming material, but silicon halides such as chlorides, e.g., $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, $SiCH_3Cl_3$, etc., fluorides, e.g., SiF_4, $SiHF_3$, SiH_2F_2, etc., bromides, e.g., $SiBr_4$, $SiHBr_3$, etc., iodides, e.g., SiI_4, etc., or alkoxysilanes expressed by $R_nSi(OR)_{4-n}$ (here, R is a C_{1-4} alkyl group, and n is an integer of 0-3) are exemplified. In addition, as the aforementioned substrate, a seed rod of a quartz glass (e.g., seed rod described in Japanese Kokoku Patent No. Sho 63[1988]-24973) can be used. In addition, a plate-form substrate may be used without restriction instead of a rod-form substrate. In addition, in the ratio of oxygen gas to hydrogen gas, an oxygen excess environment is preferred since reduction defects form in a hydrogen excess environment, and in specific a ratio of hydrogen gas to oxygen gas of 1.6-1.9 is preferred.

Next, in process (b), the aforementioned porous quartz glass body is kept in a fluorine-containing environment at a temperature of 600°C or lower to obtain a fluorine-containing porous quartz glass body. As the fluorine-containing environment, an inert gas environment containing 0.1-100 vol% and especially 1-20 vol% of fluorine-containing gas (e.g., SiF_4, SF_6, CHF_3, CF_4, F_2) is preferred. It is preferred to treat a porous quartz glass body in the aforementioned environment at a temperature of 600°C or less and a pressure of 1-10 atm for several tens of minutes to several hours. In addition, when fluorine is doped at a high temperature of 500-1000°C, an environment containing 5-90% oxygen is preferably used to suppress the formation of reduction defects. Furthermore, "atm" and "torr" in this specification are not gage pressure but absolute pressure.

Furthermore, in process (b), since a porous quartz glass body can be uniformly doped with fluorine in a short time, it is preferred to prepare the fluorine-containing environment with a temperature of 1200°C or less and preferably 600°C or less and a reduced pressure (preferably 100 torr or less, particularly 10 torr or less) and to feed a fluorine-containing gas into it.

Next, in process (c), the aforementioned fluorine-containing porous quartz glass body is heated in an environment containing practically no fluorine to a temperature of transparency-forming vitrification to vitrify to obtain a fluorine-containing transparent glass body. The transparency-forming vitrification temperature is 1300°C or higher, preferably 1300-1600°C, further preferably 1350-1500 C.

. As the environment containing practically no fluorine gas, as long as it contains 0.1 vol% or less of a fluorine-containing gas (e.g., SiF_4, SF_6, CHF_3, CF_4, F_2) at the initiation of the treatment by process (c), it is not particularly restricted, and an environment of 100% inert gas such as helium or an environment containing an inert gas such as helium as a main component is preferred. In addition, as the pressure, a reduced pressure or normal pressure is sufficient. Especially in the case of normal pressure, helium gas can be used. In addition, a pressure of 100 torr or less and especially 10 torr or less is preferred.

In addition, it is preferred to have a process (e) of reducing the environment pressure and keeping the fluorine-containing porous quartz glass body under the reduced pressure for a prescribed time between process (b) and process (c). In specific, it is preferred to have a process of keeping the fluorine-containing porous quartz glass in an inert gas environment at the fluorine doping temperature of process (b) and a pressure of 100 torr or less and preferably 10 torr or less for several tens of minutes to several hours. It is necessary to remove fluorine from the environment after process (b). Fluorine can be removed in a short time at a reduced pressure as in process (e), but it takes a long time at normal pressure although this is also allowed.

Next, in process (d), the fluorine-containing transparent quartz glass body obtained in process (c) is heated in a hydrogen gas-containing environment at a temperature of 600° or less to obtain a synthetic quartz glass. The pressure is, e.g., 1-30 atm. The formation of reduction defects of ≡Si-H and ≡Si-Si≡ can be prevented by treating with hydrogen at 600°C or lower. As the hydrogen gas-containing environment, an inert gas environment containing 0.1-100 vol% of hydrogen gas is preferred. Furthermore, it is preferred for control of the virtual temperature to conduct the process (f) described below on the transparent quartz glass body.

(f) The fluorine-containing transparent glass body is kept at a temperature of 800-1100°C for at least 5 h and then the temperature is lowered to 750°C or lower at a temperature dropping rate of 10°C/h or less to control the virtual temperature of the synthetic quartz glass.

After the temperature is lowered to 750°C or less, it can be naturally cooled. In this case, the environment is a 100% inert gas such as helium, argon, nitrogen, etc., an inert gas-based environment, or air, and the pressure may be a reduced pressure or normal pressure.

In addition, a synthetic quartz glass of the present invention may be produced by holding the porous quartz glass body obtained in process (a) at a pressure of 1 torr or less and a temperature of 1000-1300°C for a prescribed time and executing process (e) of vitrifying by heating at a pressure of 1 torr or less to the transparency-forming, vitrification temperature.

The synthetic quartz glass of the present invention is used for stepper lenses and other optical components. It is necessary for endowing optical characteristics required for optical components to suitably carry out the heat treatments of homogenizing, molding, and annealing

(hereinafter called optical heat treatment), and the optical heat treatment may be carried out before or after process (d).

Since a high temperature of 800-1500°C is needed for optical heat treatment, however, even if hydrogen is contained in the process (d), there is a possibility of lowering the hydrogen molecule concentration by the subsequent optical heat treatment. Therefore, when the optical heat treatment is carried out after process (d), it is preferred to carry it out under an environment containing 0.1-100 vol% of hydrogen gas at a pressure of 1-30 atm.

In addition, when the optical heat treatment is carried out after process (d), it is necessary for the furnace for the optical heat treatment to be an anti-explosion structure. Therefore, it is preferred to carry out the optical heat treatment before process (d).

In the present invention, a large amount of fluorine can be doped by doping boron. In the case of boron doping, as a boron source, BF_3, BCl_3, and boron alkoxide are examples.

In addition, as a method for doping boron and fluorine, for instance, a method of first doping with boron and then doping with fluorine is an example.

In specific, boron and fluorine are doped by a method described in (1) or (2) below.

(1) The porous quartz glass body obtained in process (a) is set in a pressure vessel, and after the internal pressure of the pressure vessel is reduced to about 1 torr a gas containing a boron source (e.g., BCl_3 vapor diluted by an inert gas such as He to about 5 vol%) is fed into the pressure vessel.

When the pressure reaches approximately normal pressure, the feeding of the boron source-containing gas is stopped, and the glass body is allowed to stand for a prescribed time to dope the porous quartz glass body with boron.

Then, it is doped with fluorine according to process (b).

(2) The porous quartz glass body obtained in process (a) is treated with boron alkoxide vapor, and then the boron alkoxide is hydrolyzed in a moist environment to precipitate B_2O_3 fine particles in the porous quartz glass body.

Then, the quartz is doped with fluorine according to process (b).

The porous quartz glass body doped with boron by the method of (1) or (2) can be doped with fluorine, and moreover a large amount of fluorine can be doped. After doping with fluorine, a synthetic quartz glass for optical components can be obtained according to processes (c) and (d).

Furthermore, the fluorine doping in this case is carried out by the following steps of procedure.

An inert gas (e.g., He or N_2, etc.) is fed into the aforementioned pressure vessel until the pressure reaches normal pressure. Again, the pressure of the pressure vessel is reduced to about 1 torr, and a SiF_4 gas diluted with an inert gas (e.g., He, etc.) is fed into the pressure vessel.

·. When the pressure reaches approximately normal pressure, the feeding of the inert gas-diluted SiF_4 gas is stopped, and the vessel is allowed to stand for a prescribed time to dope the boron-containing porous quartz glass body with fluorine.

Hereinafter, the present invention is explained in detail by application examples, but the present invention is not limited to those only. Furthermore, synthetic quartz glasses prepared in those examples were evaluated by the following methods.

(Evaluation)
(Evaluation 1) Measurement of fluorine concentration

A synthetic quartz glass is heated and melted by anhydrous sodium carbonate, and distilled water and hydrochloric acid (volume ratio 1:1) are added to the resulting melt to prepare a sample liquid. The electromotive force of the sample liquid is measured by a radiometer with No. 945-220 and No. 945-468 of Radiometer Trading Co. as a fluorine ion selective electrode and a control electrode, respectively, to determine the fluorine concentration based on a calibration curve obtained using a fluorine ion standard solution (J. of Japanese Chemical Society, 1972(2), 350).

(Evaluation 2) Measurement of hydrogen molecule concentration

The hydrogen molecule concentration (molecules/cm^3) is determined by a ratio of the intensity of the scattering peak at 4135 cm^{-1}, I_{4135}, to that of the scattering peak at 800 cm^{-1}, I_{800}, that is I_{4235}/I_{800}, in a Raman spectrum by Raman spectral measurement (V.S. Khotimchenko et al., Zhurnal Prikladnoi Spektroskopii, 46(6), 987-997 (1986)). Furthermore, the detection limit by this method is 1×10^{16} molecules/cm^3.

(Evaluation 3) Measurement of OH group concentration

The measurement is carried out by an infrared spectrophotometer, and the OH concentration is determined from the absorption peak at a wavelength of 2.7 μm (J. P. Williams et al., Ceram. Bull., 55 (5), 524 (1976)).

(Evaluation 4)

The concentration of $\equiv$Si-H defects ($\equiv$Si-H concentration) was determined from the quotient (I_{2250}/I_{800}) obtained by dividing the intensity of the scattering peak at 2250 cm^{-1}, I_{2250}, by the intensity of the scattering peak at 800 cm^{-1}, I_{800}, in a Raman spectrum by Raman spectral measurement. Here, the detection limit is $I_{2250}/I_{800} = 1 \times 10^{-4}$. A small I_{2250}/I_{800} value is a good result.

(Evaluation 5)

The light transmittances at 245 nm of a 10 mm-thick sample and a 35 mm-thick sample were measured using an ultraviolet visible spectrophotometer, and the absorption coefficient at 245 nm was calculated from those transmittances to evaluate the formation of $\equiv$Si-Si$\equiv$ defects. A small absorption coefficient at 245 nm is a good result.

(Evaluation 6) Reduction defects

The light transmittances at a wavelength of 163 nm of a 10 mm-thick sample and a 4 mm-thick sample were measured using a vacuum ultraviolet spectrophotometer (VTMS-502, Acton Research Co.), and the absorption coefficient at a wavelength of 163 nm (k_{163}) was determined from the measurement results. When the OH group concentration (C_{OH}, unit: ppm) in the sample satisfied $k_{163} \geq 0.02 \times (C_{OH})^{0.85}$ the sample was judged to contain reduction defects while when it did not satisfy the above, it was judged to contain no reduction defects.

(Evaluation 7)

A sample was irradiated with a KrF excimer laser (LPX-120i, Lambda Physics Co.) under the conditions of an energy density of 100 mJ/cm^2/pulse and a frequency of 200 Hz. The transmittance at 214 nm immediately after 5×10^6 shots of irradiation of the KrF excimer laser beam was measured by an ultraviolet visible spectrophotometer, and the 214 nm absorption intensity by paramagnetic defect E' centers caused by KrF excimer laser irradiation was evaluated by the change in the absorption coefficient before and after irradiation Δk_{214} [cm^{-1}]. A small Δk_{214} value indicates the reduction of E' centers and it is a good result.

(Evaluation 8) Evaluation of fluorescence illumination

A sample was irradiated with a KrF excimer laser (LPX-120i, Lambda Physics Co.) under the conditions of an energy density of 100 mJ/cm^2/pulse and a frequency of 200 Hz. In the case of 1×10^6 shots of irradiation of the KrF excimer laser, the fluorescence intensity at 650 nm, L_{650}, and the scattering light intensity at 248 nm, S_{248}, were measured using a fiber type spectrophotometer, and the fluorescence intensity at 650 nm was evaluated by determining the ratio, L_{650}/S_{248}, of fluorescence intensity at 650 nm, L_{650}, to scattering light intensity at 248 nm, S_{248}. A small L_{650}/S_{248} value shows suppression of fluorescent illumination, and it is a good result.

(Evaluation 9) Internal transmittance at 172 nm

On a 10 mm-thick sample and a 4 mm-thick sample, the internal transmittance at 172 nm, as an index of transmittance in the vacuum ultraviolet region at a wavelength of 175 nm or less, was measured using a vacuum ultraviolet spectrophotometer (VTMS-502, Acton Research Co.).

(Evaluation 10) Internal transmittance at 157 nm

On a 10 mm-thick sample and a 4 mm-thick sample, the internal transmittance at 157 nm, as an index of the transmittance in the vacuum ultraviolet region at a wavelength of 160 nm or less, was measured using a vacuum ultraviolet spectrophotometer (VTMS-502, Acton Research Co.), and internal transmittance at the same wavelength was determined by the following equation.

Internal transmittance (%/cm) = exp (-ln $(T_1/T_2)/(d_1-d_2)$) x 100

where T_1:   transmittance (%) of a sample with a thickness d_1 [cm]

     T_2:   transmittance (%) of a sample with a thickness d_2 [cm]

Those having a high transmittance indicate a good result.

(Evaluation 11)

A sample with a thickness of 10 mm was irradiated with an Xe_2° excimer lamp at 10 mW/cm^2. The transmittance at 163 nm was measured before and after irradiation, and change of transmittance at 163 nm (ΔT_{163}) by irradiation was calculated. The UV resistance is improved as ΔT_{163} decreases.

(Evaluation 12) Measurement of virtual temperature

The virtual temperature was measured using the method of A. Agarwal et al. (J. Non-Cryst., 185, 191, 1995). A quartz glass polished to a mirror surface is dipped in 10% HF-2.5% H_2SO_4 aqueous solution to remove residual abrasives and scratches. The reflection spectra of its surface are obtained by an infrared spectrometer (Magna 760, Nikolet Co.). At this time, the infrared incident angle is fixed at 6.5 degrees and the data interval is about 0.5 cm^{-1}, and then an average value from 64 time scans is used. In the infrared reflection spectra thus obtained, the largest peak observed at about 1120 cm^{-1} is originated in the stretching vibration by the Si-O-Si bond in the quartz glass. If the position of this peak is expressed by v (cm^{-1}), the virtual temperature (T_f, unit: K) is determined by the following correlation equation.

$v = 1114.51 + (11603.51/T_f)$

(Evaluation 13) Measurement of chlorine concentration

The characteristic x-ray intensity of chlorine was measured by fluorescence x-ray analysis using the $k\alpha$ line of Cr to determine the chlorine concentration in synthetic quartz glass. Furthermore, the detection limit in this method is 2 ppm.

(Evaluation 14) Evaluation of unstable structure

The ratio, I_1/I_0, of the intensity of the scattering peak at 495 cm^{-1} (I_1) to that of the scattering peak at 440 cm^{-1} (I_0) and also the ratio, I_2/I_0, of the intensity of the scattering peak at 605 cm^{-1} (I_2) to that of the scattering peak at 440 cm^{-1} (I_0) in a laser Raman spectrum were determined by Raman spectral measurement (Ramonor T64000, Jobin Ybon Co., excitation source: argon ion laser (wavelength 514.5 nm). It is better as the intensity ratio I_1/I_0 and the intensity ratio I_2/I_0 decrease.

Each scattering peak I_1, I_2, I_0 is determined by the following method

For the scattering peak at 495 cm^{-1} and the scattering peak at 605 cm^{-1}, curve fitting was conducted by respective Lorentz functions and an approximation of the least squares error with the actual spectra minimum was carried out to determine the coefficient of each function.

Curve fitting was conducted by synthesis of three Gauss functions for the scattering peak at 440 cm^{-1} and by a second order function for the remainder (baseline) excluding the scattering peak at 495 cm^{-1}, the scattering peak at 605 cm^{-1}, and the scattering peak at 440 cm^{-1}, and an approximation of the least squares error with the actual spectra minimum were carried out to determine the coefficient of each function.

The intensity of each scattering peak was determined using the functions thus obtained.

(Evaluation 15)

The concentrations of Na, Ca, Mg, Fe, Ni, Cu, Zn, and Ti in a synthetic quartz glass were analyzed by the ICP mass analytical method (SPQ9000, Seiko Instruments Co.). The detection limits for those impurities are 0.1 ppb for Ni and Cu and 0.3 ppb for the others.

(Evaluation 16)

A refractive index distribution in a 200 mmφ plane of a synthetic quartz glass sample was measured by vertically applying a helium-neon laser beam to the 200 mmφ plane using a Fizeau interferometer according to the oil-on-plate method.

Example 1

Quartz glass fine particles, obtained by heating and hydrolyzing (flame hydrolysis) $SiCl_4$ as a quartz glass forming raw material in an oxyhydrogen flame according to a known method,

were deposited and grown on a substrate to form a porous quartz glass body with a diameter of 35 cm and a length of 100 cm (process (a)). The porous quartz glass body was set in an environment controllable electric furnace, and after reducing the pressure at room temperature to 10 torr and holding the porous quartz glass body for 1 h, fluorine doping was carried out by holding the porous quartz glass body in an environment at room temperature and normal pressure for 5 h with feeding of a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) (process (b)). Then, the SiF$_4$ feeding was stopped, and the quartz was kept in a 100% He environment for 10 h, heated in the 100% He environment to 1450°C, and vitrified to transparency by holding it at that temperature for 10 h to obtain a fluorine-containing transparent glass body (process (c)).

The fluorine-containing transparent quartz glass body was dead load deformed in an electric furnace having carbon heating elements by heating to 1750°C, which was higher than the softening temperature, to obtain a block of 250 mm x 250 mm x 120 mm and sliced to a block with a thickness of 30 mm. The 250 mm x 250 mm x 30 mm block was doped with hydrogen by holding it in 100% hydrogen at 10 atm and 500°C for 150 h to obtain a synthetic quartz glass (process (d)).

Example 2

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 300°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) into the electric furnace and keeping it at 300°C under atmospheric pressure for 5 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 3

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 500°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) into the electric furnace and keeping it at 500°C under atmospheric pressure for 5 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 4

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 700°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) into the electric furnace and keeping it at 700°C under atmospheric pressure for 5 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 5

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 1200°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of $He/SiF_4 = 99/1$ (volume ratio) into the electric furnace and keeping it at 1200°C under atmospheric pressure for 5 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 6

In the process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 300°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of $He/SiF_4 = 99.9/0.1$ (volume ratio) into the electric furnace and keeping it at 300°C under atmospheric pressure for 1 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 7

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 300°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of $He/SiF_4 = 99.9/0.1$ (volume ratio) into the electric furnace and keeping it at 300°C and 300 torr for 1 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 8

In process (b) of Example 1, the porous quartz glass body was set in an electric furnace, first heated to 300°C, kept at that temperature for 1 h after reducing the pressure to 10 torr, and doped with fluorine by introducing a mixed gas of $He/SiF_4 = 99.9/0.1$ (volume ratio) into the electric furnace and keeping it at 300°C and 100 torr for 1 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 9

In process (d) of Example 1, the hydrogen doping was carried out by holding in a 100% hydrogen environment at 1 atm and a temperature of 500°C for 250 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 10

In process (d) of Example 1, the hydrogen doping was carried out by holding in a mixed gas of hydrogen/helium = 10/90 (volume ratio) at 1 atm and a temperature of 500°C for 250 h.

Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 11

In process (d) of Example 1, the hydrogen doping was carried out by holding in a 100% hydrogen environment at 10 atm and a temperature of 700°C for 250 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 12

In process (d) of Example 1, the hydrogen doping was carried out by holding in a 100% hydrogen environment at 10 atm and a temperature of 900°C for 250 h. Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 13

At process (b) of Example 1, the porous quartz glass body was vitrified to transparency by heating to 1450°C in a 100% helium environment and keeping at that temperature for 10 h without carrying out process (b). Except for this, by the same method as that in Example 1, a synthetic quartz glass was manufactured.

Example 14

After carrying out process (b) in Example 1, the feeding of SiF_4 was stopped, and the pressure was kept at 1 torr for 1 h after reducing it to that level (process (e)). Then, 100% He was introduced to restore the pressure to normal pressure, and the pressure was again reduced to 1 torr to obtain a fluorine-free environment. The quartz was heated to 1450°C in the fluorine-free environment, kept at 1450°C for 10 h, and vitrified to transparency to obtain a fluorine-containing transparent quartz glass body (process (c)). After this, it was treated in the same manner as that in Example 1 to obtain a synthetic quartz glass.

Example 15

After carrying out process (b) in Example 1, the feeding of SiF_4 was stopped, and the quartz was kept in a 100% He environment for 10 h, further kept in a mixed gas environment of $He/SiF_4 = 99.95/0.05$ (volume ratio) for 10 h, heated to 1450°C, kept at 1450°C for 10 h, and vitrified to transparency to obtain a fluorine-containing transparent quartz glass body (process (c)). After this, it was treated in the same manner as that in Example 1 to obtain a synthetic quartz glass.

Example 16

After carrying out process (b) in Example 1, the feeding of SiF_4 was stopped, and the quartz was kept in a 100% He environment for 10 h, further kept in a mixed gas environment of $He/SiF_4 = 99.8/0.2$ (volume ratio) for 10 h, heated to 1450°C, kept at 1450°C for 10 h, and vitrified to transparency to obtain a fluorine-containing transparent quartz glass body (process (c)). After this, it was treated in the same manner as that in Example 1 to obtain a synthetic quartz glass.

The synthetic quartz glass samples obtained in Examples 1-16 were evaluated. Evaluation results are shown in Table 1. ND means that it is below the detection limit. Furthermore, Examples 1-3, Examples 6-10, and Examples 14-15 are application examples while Examples 4-5, Examples 11-13 and Example 16 are comparative examples.

Table 1

例	評価1 フッ素濃度 (ppm)	評価2 水素濃度 [分子／cm³]	評価3 OH濃度 (ppm)	評価4 ≡Si−H濃度 (I_{2260}/I_{800}) [−]	評価5 245nm 吸収係数 [cm⁻¹]	評価6 163nm 吸収の有無	評価7 Δk_{211} [cm⁻¹]	評価8 蛍光強度比 L_{211}/S_{211} [−]
1	816	2.9×10^{18}	5.1	$<1\times10^{-4}$	7.2×10^{-4}	無し	8.0×10^{-3}	3.1×10^{-5}
2	983	3.0×10	3.8	$<1\times10^{-4}$	7.4×10^{-4}	無し	8.1×10^{-3}	2.0×10^{-5}
3	1161	3.0×10^{18}	3.2	$<1\times10^{-4}$	7.6×10^{-4}	無し	9.0×10^{-3}	2.1×10^{-5}
4	2219	2.9×10^{18}	1.9	$<1\times10^{-4}$	2.3×10^{-3}	有り	6.2×10^{-1}	2.5×10^{-5}
5	10412	2.9×10^{18}	ND	$<1\times10^{-4}$	4.7×10^{-2}	有り	1.5×10^{0}	1.5×10^{-5}
6	325	2.8×10^{18}	12	$<1\times10^{-4}$	7.4×10^{-4}	無し	8.0×10^{-3}	6.2×10^{-5}
7	150	3.0×10^{18}	40	$<1\times10^{-4}$	7.5×10^{-4}	無し	8.1×10^{-3}	1.3×10^{-4}
8	50	3.0×10^{18}	110	$<1\times10^{-4}$	7.4×10^{-4}	無し	8.2×10^{-3}	2.5×10^{-4}
9	816	2.8×10^{17}	5.2	$<1\times10^{-4}$	7.3×10^{-4}	無し	1.6×10^{-2}	3.5×10^{-5}
10	816	2.5×10^{18}	5.3	$<1\times10^{-4}$	7.4×10^{-4}	無し	3.2×10^{-2}	3.3×10^{-5}
11	816	1.8×10^{18}	5.0	6.8×10^{-3}	7.2×10^{-4}	無し	2.7×10^{-1}	3.3×10^{-5}
12	816	1.3×10^{18}	5.1	1.0×10^{-2}	7.3×10^{-4}	無し	3.2×10^{-1}	3.4×10^{-5}
13	0	2.9×10^{18}	400	$<1\times10^{-4}$	7.3×10^{-4}	無し	9.0×10^{-3}	9.8×10^{-4}
14	816	3.0×10^{18}	5.6	$<1\times10^{-4}$	7.3×10^{-4}	無し	7.8×10^{-3}	2.7×10^{-5}
15	816	2.9×10^{18}	4.3	$<1\times10^{-4}$	7.3×10^{-4}	無し	7.8×10^{-3}	3.0×10^{-5}
16	913	2.9×10^{18}	2.1	$<1\times10^{-4}$	2.5×10^{-3}	有り	6.5×10^{-1}	2.7×10^{-5}

Key:
1. Examples
2. Evaluation
3. Fluorine concentration
4. Hydrogen concentration (molecules/cm³)
5. OH concentration
6. ≡Si-H concentration
7. 245 nm Absorption coefficient
8. Presence of 163 nm absorption

9 Fluorescence intensity ratio
10 No
11 Yes

Examples 17-34 are experimental examples, wherein the effects of OH group concentration, chlorine concentration, and fluorine concentration on the characteristics of synthetic quartz glass were investigated.

Examples 17-31

SiO_2 fine particles, which were obtained by hydrolyzing $SiCl_4$ or $Si(CH_3O)_4$ in an oxyhydrogen flame at 1200-1500°C according to a known soot method, were deposited on a substrate to prepare a porous quartz glass body with a diameter of 500 mm and a length of 600 mm. Then, the porous quartz glass body was set in an environment controllable electric furnace, and helium gas containing SiF_4 at ratios shown in Table 2 was fed into the electric furnace, and then the porous quartz glass body was kept in the environment for given times shown in Table 2 to carry out dehydration of the porous quartz glass body and at the same time to dope it with fluorine. Further, it was heated to 1450°C at a reduced pressure of 10 torr or less and kept at that same temperature for 10 h to prepare a transparent quartz glass body (diameter 200 mm, length 450 mm).

Furthermore, the transparent quartz glass body was cut to a diameter of 200 mm and a thickness of 10 mm and kept in an environment containing hydrogen at amounts shown in Table 2 at 500°C and pressures shown in Table 2 for 30 h. In the above production method, the OH group concentration and fluorine concentration in the quartz glass were controlled by the ratios of the amounts of flowing oxygen gas and hydrogen gas to that of the raw material gas during the manufacture of the porous quartz glass body or by the concentration of the fluorine compound and the holding time when the porous quartz glass body was kept in the environment containing a fluorine compound. In addition, the concentration of hydrogen molecules in the quartz glass was controlled by adjusting the hydrogen concentration in the environment and the total pressure when the quartz glass body was kept in the hydrogen environment. Furthermore, the detailed production conditions (ratio of amounts of the glass forming raw material, oxygen, and hydrogen gas, fluorine compound concentration and pressure, hydrogen concentration and pressure) are shown in Table 2.

Table 2

例	製法	ガラス形成原料	火炎加水分解条件（ガラス形成原料を基準にしたときのO_2／H_2体積比率）	フッ素ドープ条件（フッ素濃度・時間）		水素ドープ条件（水素濃度・圧力）	
17	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	10hr	H_2=100vol%	10atm
18	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	3hr	H_2=100vol%	10atm
19	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	2hr	H_2=100vol%	10atm
20	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	1hr	H_2=100vol%	10atm
21	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	30min	H_2=100vol%	10atm
22	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	5min	H_2=100vol%	10atm
23	スート法	$SiCl_4$	15／25	処理なし		H_2=100vol%	10atm
24	スート法	$Si(CH_3O)_4$	0／0	SiF_4/He=1/99vol%	3hr	H_2=100vol%	10atm
25	スート法	$SiCl_4$	11／30	SiF_4/He=1/99vol%	3hr	H_2=100vol%	10atm
26	スート法	$SiCl_4$	13／27	SiF_4/He=1/99vol%	3hr	H_2=100vol%	10atm
27	スート法	$SiCl_4$	16／22	SiF_4/He=1/99vol%	3hr	H_2=100vol%	10atm
28	スート法	$SiCl_4$	15／25	SiF_4/$SiCl_4$/He=1/0.01/98.99vol%	1hr	H_2=100vol%	10atm
29	スート法	$SiCl_4$	15／25	SiF_4/$SiCl_4$/He=1/0.2/99.98vol%	1hr	H_2=100vol%	10atm
30	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	3hr	H_2=100vol%	5atm
31	スート法	$SiCl_4$	15／25	SiF_4/He=1/99vol%	3hr	H_2/He=10/90vol%	1atm

Key: 1   Example
2   Preparation method
3   Glass forming raw material
4   Flame hydration condition
     (O_2/H_2 volume ratio based on the glass forming raw material)
5   Fluorine doping condition
     (fluorine concentration, time)
6   Hydrogen doping condition
     (hydrogen concentration, pressure)
7   Soot method
8   Not treated

Examples 32-34

SiCl₄, as a glass forming raw material, with SiF_4, oxygen, and hydrogen gas, the feeding ratios of which with respect to the raw material gas are shown in Table 3, was hydrolyzed and oxidized in an oxyhydrogen flame at 1800-2000°C according to a known direct method to

directly prepare a transparent quartz glass body on a substrate. In this preparation method, the fluorine concentration in the quartz glass was controlled by adjusting the mixing ratio of $SiCl_4$ and SiF_4, further the OH group concentration and hydrogen concentration were controlled by controlling the flow ratios of oxygen and hydrogen. Furthermore, the detailed preparation conditions (SiF_4, flow ratio of oxygen and hydrogen) are shown in Table 3.

Table 3

例	製法	ガラス 形成原料	火炎加水分解条件 （ガラス形成原料を基準にした SiF₄／O₂／H₂体積比率）
32	直接法	SiCl₄	0. 8／1 4 0／2 0 0
33	直接法	SiCl₄	0. 8／8 0／8 0 0
34	直接法	SiCl₄	0. 0／1 5 0／2 0 0

Key:　1　　　Example
　　　　2　　　Preparation method
　　　　3　　　Glass forming raw material
　　　　4　　　Flame hydrolysis condition
　　　　　　　($SiF_4/O_2/H_2$ volume ratio based on the
　　　　　　　glass forming raw material)
　　　　5　　　Direct method

The OH group concentration, chlorine concentration, fluorine concentration, and hydrogen molecule concentration of synthetic quartz glass samples prepared in Examples 17-34 are shown in Table 4. Furthermore, concentrations were determined by the aforementioned methods, and ND means less than the detection limit.

Table 4

例	OH基濃度 （ppm）	塩素濃度 （ppm）	フッ素濃度 （ppm）	水素分子濃度 ［分子／cm³］
17	5.5	7.2	913	1.8×10^{18}
18	21	7.0	873	1.8×10^{18}
19	46	6.9	864	1.9×10^{18}
20	73	6.8	835	1.8×10^{18}
21	118	7.0	639	1.9×10^{18}
22	230	7.1	369	1.8×10^{18}
23	39	7.2	ND	1.8×10^{18}
24	21	ND	866	1.8×10^{18}
25	20	6.8	114	1.8×10^{18}
26	22	6.7	220	1.8×10^{18}
27	21	6.9	1860	1.8×10^{18}
28	21	61	873	1.8×10^{18}
29	19	134	462	1.9×10^{18}
30	21	7.0	854	5.4×10^{17}
31	20	7.1	829	1.8×10^{16}
32	950	72	1271	3.1×10^{18}
33	45	73	1293	3.1×10^{18}
34	930	68	ND	3.1×10^{18}

Key: 1   Example
2   OH group concentration
3   Chlorine concentration
4   Fluorine concentration
5   Hydrogen molecule concentration [molecules/cm³]

Next, the synthetic glass samples prepared in Examples 17-34 were evaluated by measuring respective scattering peak intensity ratios (I_1/I_0, I_2/I_0), Δk_{214}, L_{650}/S_{248}, internal transmittance at a wavelength of 157 nm, and impurity concentration in the synthetic quartz glass samples. Evaluation results are shown in Table 5. Among Examples 17-34, those mentioned below were inferior in characteristics compared to others because Examples 20, 21, 22, 32, and 34 had high OH group concentrations, Example 29 had a high chlorine concentration, and Examples 23, 24 did not contain fluorine.

Table 5

例	評価1		評価2	評価3	評価4	評価5
	I_1/I_0 [-]	I_2/I_0 [-]	Δk_{214} [cm^{-1}]	L_{650}/S_{214} [-]	③157nmにおける透過率 (%/cm)	不純物濃度 (ppb)
17	0.560	0.123	6.03×10^{-3}	1.8×10^{-5}	78.1	すべてND
18	0.560	0.123	6.05×10^{-3}	3.6×10^{-5}	54.4	すべてND
19	0.560	0.123	6.13×10^{-3}	5.1×10^{-5}	35.6	すべてND
20	0.559	0.123	6.03×10^{-3}	6.7×10^{-5}	24.4	すべてND
21	0.562	0.124	6.05×10^{-3}	8.4×10^{-5}	14.2	すべてND
22	0.564	0.125	6.07×10^{-3}	1.2×10^{-4}	4.7	すべてND
23	0.589	0.138	1.56×10^{-2}	3.6×10^{-5}	39.7	すべてND
24	0.561	0.123	5.98×10^{-3}	3.6×10^{-5}	54.4	すべてND
25	0.568	0.129	8.84×10^{-3}	3.6×10^{-5}	55.5	すべてND
26	0.566	0.128	8.16×10^{-3}	3.7×10^{-5}	53.4	すべてND
27	0.543	0.115	5.48×10^{-3}	3.6×10^{-5}	54.4	すべてND
28	0.560	0.123	9.38×10^{-3}	3.7×10^{-5}	54.4	すべてND
29	0.570	0.128	4.03×10^{-1}	3.6×10^{-5}	56.6	すべてND
30	0.561	0.124	7.56×10^{-3}	4.5×10^{-5}	54.4	すべてND
31	0.562	0.124	2.43×10^{-2}	1.6×10^{-4}	55.5	すべてND
32	0.516	0.101	1.51×10^{-2}	2.6×10^{-4}	<0.1	すべてND
33	0.515	0.103	1.45×10^{-2}	3.6×10^{-5}	36.1	すべてND
34	0.552	0.119	1.61×1.0^{-2}	2.5×10^{-4}	<0.1	すべてND

Key:
1 Example
2 Evaluation
3 Transmittance at 157 nm
4 Impurity concentration
5 All ND

Examples 35-47 are experimental examples where the effects of I_1/I_0 and I_2/I_0 on the characteristics of synthetic quartz samples were investigated.

Examples 35-47

SiO_2 fine particles, which were obtained by hydrolyzing $SiCl_4$ in an oxyhydrogen flame according to a known soot method, were deposited on a substrate to prepare a 500 mmφ x length 600 mm porous quartz glass body (process (a)). The porous quartz glass body was set in an

environment controllable electric furnace, and helium gas containing a fluorine compound was fed into the electric furnace at room temperature and a reduced pressure of less than 10 torr until the pressure reached normal pressure. The porous quartz glass was kept in this environment for several hours to simultaneously carry out dehydration and fluorine doping (process (b)). Then, it was heated under a reduced pressure of less than 10 torr to 1450°C and kept at this temperature for 10 h to obtain a transparent quartz glass body (200 mmφ x length 450 mm).

Furthermore, the transparent quartz glass body was cut to 200 mmφ x thickness 10 mm and kept in a hydrogen-containing environment at 500°C under the conditions shown in Table 6 for 30 h to dope with hydrogen to obtain the synthetic quartz glass samples of Examples 35-47 shown in Table 7 (process (c)).

In the aforementioned method, the OH group concentration and fluorine concentration in the quartz glass were controlled by controlling the flow ratios of oxygen and hydrogen gas to the raw material gas in process (a) and the concentration of the fluorine compound and treating time in process (b). In addition, the hydrogen molecule concentration in the quartz glass was controlled by controlling the hydrogen concentration in the environment and total pressure during hydrogen treatment in process (c). Furthermore, detailed treatment conditions in process (a), process (b), and process (c) of each example are shown in Table 6.

Table 6

	工程 (a) 合 成 条 件 （ガラス形成原料を基準にしたときのO₂／H₂体積比率）	工程 (b) フッ素処理条件 （雰囲気・処理時間）	工程 (d) 水素処理条件 （雰囲気・圧力）
例35	14／26	SiF₄/He＝1/99vol%・5min	H₂＝100vol%・10atm
例36	14／26	SiF₄/He＝1/99vol%・10min	H₂＝100vol%・10atm
例37	13／27	SiF₄/He＝1/99vol%・30min	H₂＝100vol%・10atm
例38	14／26	SiF₄/He＝1/99vol%・30min	H₂＝100vol%・10atm
例39	15／25	SiF₄/He＝1/99vol%・3hr	H₂＝100vol%・10atm
例40	15／25	SiF₄/He＝1/99vol%・3hr	H₂＝100vol%・10atm
例41	15／25	SiF₄/He＝1/99vol%・3hr	H₂＝100vol%・10atm
例42	16／22	SiF₄/He＝1/99vol%・3hr	H₂＝100vol%・10atm
例43	15／20	SiF₄/He＝1/99vol%・3hr	H₂＝100vol%・1atm
例44	15／25	SiF₄/He＝1/99vol%・3hr	H₂/He＝15/85vol%・1atm
例45	14／26	SiF₄/He＝0.5/99.5vol%・5min	H₂＝100vol%・10atm
例46	15／25	処理無し	H₂＝100vol%・10atm
例47	13／25	処理無し	H₂＝100vol%・10atm

Key: 1 Process
2 Synthesis condition
(O₂/H₂ volume ratio based on glass forming raw material)
3 Fluorine treatment condition
(environment, treating time)
4 Hydrogen treatment condition
(environment, pressure)
5 Example
6 No treatment

Next, on the samples from the synthetic quartz glasses of Examples 35-47, the OH group concentration, fluorine concentration, and hydrogen molecule concentration were measured by the following shown methods. In addition, the scattering intensity ratios (I_1/I_0, I_2/I_0), Δk_{214}, L_{650}/S_{248}, and internal transmittance at a wavelength of 157 nm were measured to evaluate the

samples. Evaluation results are shown in Table 7. Among Examples 35-47, those of Examples 45-47 were inferior in characteristics compared to the others since I_1/I_0 and I_2/I_0 were high.

Table 7

	フッ素濃度 (ppm)	水素濃度 〔分子/cm³〕	OH基濃度 (ppm)	評価 2		評価2	評価3
				I_1/I_0 〔−〕	I_2/I_0 〔−〕	Δk_{211} 〔cm⁻¹〕	157nm 内部透過率 (%/cm)
例35	130	1.8×10^{18}	241	0.584	0.136	9.10×10^{-3}	4.3
例36	220	1.8×10^{18}	135	0.580	0.134	8.03×10^{-3}	11.9
例37	220	1.8×10^{18}	38	0.580	0.134	8.35×10^{-3}	40.4
例38	410	1.8×10^{18}	43	0.572	0.131	6.40×10^{-3}	37.3
例39	815	1.7×10^{18}	13.8	0.561	0.127	6.15×10^{-3}	63.3
例40	1014	1.8×10^{18}	6.8	0.557	0.125	5.98×10^{-3}	75.3
例41	1076	1.8×10^{18}	3.2	0.555	0.125	5.52×10^{-3}	84.3
例42	2274	1.8×10^{18}	1.2	0.535	0.116	5.37×10^{-3}	91.5
例43	1013	1.7×10^{17}	6.7	0.557	0.125	1.12×10^{-2}	75.5
例44	1013	1.7×10^{16}	5.6	0.557	0.125	2.29×10^{-2}	77.9
例45	45	1.8×10^{18}	213	0.588	0.137	1.28×10^{-2}	5.5
例46	0	1.8×10^{18}	198	0.590	0.138	1.62×10^{-2}	6.3
例47	0	1.8×10^{18}	33	0.591	0.140	1.68×10^{-2}	43.9

Key: 1   Evaluation
2   Fluorine concentration
3   Hydrogen concentration (molecules/cm³)
4   OH group concentration
5   157 nm internal transmittance
6   Example

Examples 48-65 are experimental examples wherein the effects of the OH group concentration and concentration of reduction defects on the characteristics of the synthetic quartz glass were investigated.

Examples 48-60

SiO$_2$ fine particles, which were obtained by hydrolyzing SiCl$_4$ in an oxyhydrogen flame according to the soot method, were deposited on a substrate to obtain a porous quartz glass body of 400 mmϕ x length 600 mm. It was set in an environment controllable electric furnace and kept at room temperature and in a reduced pressure state of 10 torr or less, and helium gas containing SiF$_4$ was introduced into the electric furnace until the pressure reached normal pressure. The porous quartz glass body was then kept in this environment of normal pressure and room temperature for several hours to carry out dehydration of the synthetic quartz glass body. Then, it was heated to 1450°C in a fluorine-free environment at a reduced pressure state of less than 10 torr and kept at this temperature for 10 h to prepare a synthetic quartz glass (200 mmϕ x length 450 mm).

Furthermore, the synthetic quartz glass was cut to 200 mmϕ x thickness 10 mm and doped with hydrogen by holding it under conditions shown in Table 8 for 30 h.

In the aforementioned manufacturing process, the OH group concentration and reduction defect concentration in the synthetic quartz glass were controlled by controlling the volume ratios of oxygen and hydrogen gases in the oxyhydrogen flame in the preparation of the porous quartz glass body and also the concentration of the fluorine compound, treating time, and treating temperature while holding the porous glass body in the fluorine compound-containing environment. In addition, the concentration of hydrogen molecules in the synthetic quartz glass was controlled by controlling the treating temperature, hydrogen concentration in the environment, and total pressure in the hydrogen doping. Furthermore, the detailed treatment conditions in the manufacturing process of each example are shown in Table 8.

Table 8

	合成条件 (O₂／H₂ 体積比率)	フッ素処理条件 (雰囲気・処理温度・処理時間)	水素処理条件 (処理温度・雰囲気・圧力)
例48	15／25	SiF₄/He=1/99vol%・25℃・10hr	500℃・H₂=100vol%・10atm
例49	16／22	SiF₄/He=1/99vol%・25℃・10hr	500℃・H₂=100vol%・10atm
例50	15／25	SiF₄/He=1/99vol%・300℃・5hr	500℃・H₂=100vol%・10atm
例51	15／25	SiF₄/He=1/99vol%・550℃・5hr	500℃・H₂=100vol%・10atm
例52	15／25	SiF₄/He=1/99vol%・700℃・5hr	500℃・H₂=100vol%・10atm
例53	15／25	SiF₄/He=1/99vol%・900℃・5hr	500℃・H₂=100vol%・10atm
例54	15／25	SiF₄/He=1/99vol%・25℃・5hr	700℃・H₂=100vol%・10atm
例55	14／26	SiF₄/He=1/99vol%・25℃・30min	500℃・H₂=100vol%・10atm
例56	14／26	SiF₄/He=1/99vol%・25℃・10min	500℃・H₂=100vol%・10atm
例57	15／25	⑤処理無し	500℃・H₂=100vol%・10atm
例58	15／25	SiF₄/He=1/99vol%・25℃・5hr	500℃・H₂=100vol%・1atm
例59	15／25	SiF₄/He=1/99vol%・25℃・5hr	500℃・H₂/He=15/85vol%・1atm
例60	15／25	SiF₄/He=1/99vol%・25℃・10hr	処理なし

Key: 1 Synthesis condition (O₂/H₂ volume ratio)
2 Fluorine treatment condition
(environment, treating temperature, treating time)
3 Hydrogen treatment condition
(treating temperature, environment, pressure)
4 Example
5 No treatment

Examples 61-65

SiO₂ fine particles, which were obtained by hydrolyzing SiCl₄ in an oxyhydrogen flame according to the soot method, were deposited on a substrate to obtain a porous quartz glass body of 400 mmφ x length 600 mm. It was set in an environment controllable electric furnace, and under a reduced pressure of less than 1 torr was kept at 1200°C for a prescribed time, heated to 1450°C, and kept at this temperature for 10 h to prepare a synthetic quartz glass (200 mmφ x thickness 450 mm).

It was then cut to 200 mmφ x thickness 10 mm and doped with hydrogen by holding in a hydrogen-containing environment under the conditions shown in Table 9 for 30 h.

In the aforementioned manufacturing process, the concentration of OH groups and reduction defects in the synthetic quartz glass were controlled by controlling the retaining time at 1200°C. In addition, the concentration of hydrogen molecules in the synthetic quartz glass was controlled by controlling the treating temperature, hydrogen concentration in the environment, and total pressure in the hydrogen doping. Furthermore, the treatment conditions in the manufacturing process of each example are shown in detail in Table 9.

Table 9

	① ガラス化条件 (1200℃における保持時間)	水素処理条件 (処理温度・雰囲気・圧力)
例61	1 0 hr	500℃・H₂＝100vol%・10atm
例62	2 0 hr	500℃・H₂＝100vol%・10atm
例63	4 0 hr	500℃・H₂＝100vol%・10atm
例64	無 し	500℃・H₂＝100vol%・10atm
例65	2 0 hr	処 理 な し

Key: 1   Vitrification condition
         (holding time at 1200°C)
       2   Hydrogen treatment condition
         (treating temperature, environment, pressure)
       3   Example
       4   None
       5   No treatment

The OH group concentration, hydrogen molecule concentration, 163 nm internal transmittance and presence of reduction defects in the synthetic quartz glass samples obtained in Examples 48-65 were determined by aforementioned methods. In addition, the internal transmittance at 172 nm, internal transmittance at 157 nm, and ΔT_{163} as an index of the UV resistance were measured to evaluate the vacuum ultraviolet transmittance at a wavelength of 175 nm and less, the vacuum ultraviolet transmittance at a wavelength of 160 nm and less, and the UV resistance. Evaluation results are shown in Table 10. Among Examples 48-65, Examples 52-54, Examples 55-58 [sic; 55-57], and Example 64 had lower internal transmittance than others since Examples 52-54 had reduction defects, and Examples 55-58 and Example 64 had relatively high OH group concentrations.

Table 10

	OH基濃度 (ppm)	水素分子濃度 〔分子／cm³〕	163nm内部透過率 (%／cm)	還元型欠陥 の 有 無
例48	4.6	1.8×10^{18}	93.7	無 し
例49	2.7	1.8×10^{18}	96.0	無 し
例50	5.8	1.8×10^{18}	92.3	無 し
例51	5.6	1.8×10^{18}	92.5	無 し
例52	4.1	1.8×10^{18}	66.5	有 り
例53	3.8	1.8×10^{18}	15.5	有 り
例54	5.8	1.4×10^{18}	84.8	有 り
例55	13.7	1.8×10^{18}	84.8	無 し
例56	23.1	1.8×10^{18}	77.4	無 し
例57	143	1.8×10^{18}	29.8	無 し
例58	6.6	1.7×10^{17}	91.6	無 し
例59	6.5	2.1×10^{16}	91.7	無 し
例60	4.5	5×10^{16}未満	93.7	無 し
例61	7.4	1.8×10^{18}	90.7	無 し
例62	4.3	1.8×10^{18}	94.1	無 し
例63	2.8	1.8×10^{18}	95.8	無 し
例64	53	1.8×10^{18}	59.4	無 し
例65	4.2	5×10^{16}未満	94.1	無 し

Key: 1   OH group concentration
2   Hydrogen molecule concentration (molecules/cm³)
3   163 nm internal transmittance
4   Presence of reduction defects
5   Example
6   No

7   Yes
8   less than 5×10^{16}

Table 11

	評 価 1 172nm内部透過率 （％／cm）	評 価 2 157nm内部透過率 （％／cm）	評価 3 △T₁₆₃ （％／cm）
例48	93.7	80.5	ND
例49	95.8	86.0	ND
例50	92.6	77.6	ND
例51	92.8	78.1	ND
例52	77.8	73.2	0.35
例53	48.9	20.5	0.63
例54	90.4	71.3	0.10
例55	86.1	63.6	ND
例56	80.0	52.5	ND
例57	40.5	10.9	ND
例58	91.8	75.9	0.01
例59	91.9	76.1	0.05
例60	93.8	80.8	0.05
例61	91.1	74.2	ND
例62	94.1	81.3	ND
例63	95.7	85.7	ND
例64	65.6	32.2	ND
例65	94.2	81.6	0.06

Key: 1   Evaluation
      2   172 nm internal transmittance
      3   157 nm internal transmittance
      4   Example

·Examples 66-81 are experimental examples, wherein the effects of fluorine concentration, OH group concentration, virtual temperature, and reduction defects on the characteristics of synthetic quartz glass were investigated.

Examples 66-81

SiO₂ fine particles, which were obtained by hydrolyzing $SiCl_4$ as a glass forming raw material in an oxyhydrogen flame at 1200-1500°C according to a known soot method, were deposited on a substrate to obtain a porous quartz glass body of 300 mmϕ x length 800 mm. The conditions of the oxyhydrogen flame in process (a) are shown in Table 12. The process (a) column in Table 12 shows the volume ratios of oxygen and hydrogen to $SiCl_4$ as the glass forming raw material.

The porous quartz glass body was set in an environment controllable electric furnace and simultaneously dehydrated (lowering of OH groups) and doped with fluorine in process (b) in environments at treatment temperatures for treating times shown in Table 11 [sic; 12]. Furthermore, the environment in process (b) of Table 12 is expressed by volume %. It was then heated at a reduced pressure of less than 10 torr to 1450°C and kept at this temperature for 10 h to prepare a transparent quartz glass body (105 mmϕ x length 650 mm).

Furthermore, the transparent quartz glass body was heated in an electric furnace having carbon heating elements under a 100% nitrogen gas environment at normal pressure to 1750°C, which was higher than the softening point, to carry out dead load deformation along the growth axis direction to obtain a columnar block. Then, the block at the setting up state was heated at treating temperatures for treating times shown under process (d) of Table 12, and then the temperature was dropped to room temperature in a temperature dropping profile described process (d) of Table 12 to control the virtual temperature.

In the aforementioned manufacturing process, the OH group concentration and fluorine concentration in the synthetic quartz glass were controlled by controlling the flow ratios of oxygen and hydrogen to the raw material gas in the preparation of the porous quartz glass body or by controlling the environment gas composition and temperature while holding the porous quartz glass body in the fluorine compound-containing environment. In addition, the virtual temperature was controlled by controlling the temperature while holding the molded columnar block at high temperature and the temperature dropping profile.

The fluorine concentration, OH group concentration, virtual temperature, and presence of reduction defects were measured and results are shown in Table 13.

In addition, the internal transmittance at a wavelength of 157 nm as an index for the transmittance in the vacuum ultraviolet region at a wavelength of 200 nm and less was measured. Evaluation results are shown in Table 14.

Furthermore, among Examples 66-81 in Tables 12-14, those mentioned below were inferior in characteristics compared to others because Examples 66, 73 had high OH group concentrations; Example 73 had a low fluorine concentration; Example 74 had a high virtual temperature; and Example 81 contained reduction defects.

Table 12

	工程（a） 合成条件 （ガラス形成原料を 基準にしたときの酸 素／水素体積比率）	工程（b） フッ素処理条件 （雰囲気・処理温度・処理時間）	工程（d） アニール条件 （処理温度・処理時間・降温プロファイル）
例66	14／26	SiF4/He=0.5vol%/99vol%, 室温, 3hr	1000℃×100hr,700℃まで5℃/hrで降温
例67	14／26	SiF4/He=1vol%/99vol%, 室温, 15hr	1000℃×100hr,700℃まで5℃/hrで降温
例68	14／26	SiF4/He=1vol%/99vol%, 室温, 20hr	1000℃×100hr,700℃まで5℃/hrで降温
例69	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温
例70	14／26	SiF4/He=1vol%/99vol%, 500℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温
例71	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温
例72	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温
例73	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温
例74	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	無し
例75	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	1050℃×100hr,700℃まで5℃/hrで降温
例76	14／26	SiF4/He=1vol%/99vol%, 300℃, 10hr	900℃×100hr,700℃まで5℃/hrで降温
例77	14／26	SiF4/He=5vol%/95vol%, 500℃, 10hr	850℃×100hr,700℃まで5℃/hrで降温
例78	15／25	SiF4/O2/He=5vol%/20vol%/75vol%, 700℃, 10hr	850℃×100hr,700℃まで5℃/hrで降温
例79	15／25	SiF4/O2/He=5vol%/50vol%/45vol%, 900℃, 10hr	800℃×200hr,700℃まで5℃/hrで降温
例80	15／25	SiF4/O2/He=10vol%/80vol%/10vol%, 900℃, 10hr	700℃×200hr
例81	14／26	SiF4/He=5vol%/95vol%, 700℃, 10hr	1000℃×100hr,700℃まで5℃/hrで降温

Key: 1   Process
      2   Synthetic condition
           (oxygen/hydrogen volume ratio based on the glass forming raw material)
      3   Fluorine treatment condition
           (environment, treating temperature, treating time)
      4   Annealing condition
           (treating temperature, treating time, temperature dropping profile)
      5   Example
      6   Room temperature
      7   Temperature was lowered to 700°C at 5°C/h
      8   None

Table 13

	ＯＨ基濃度 （ｐｐm)	フッ素濃度 （ｐｐm)	仮想温度 [℃]	還元型欠陥の有無
例６６	17.1	150	990	無し
例６７	8.8	160	990	無し
例６８	6.4	190	990	無し
例６９	4.7	200	985	無し
例７０	3.6	200	985	無し
例７１	1.2	200	985	無し
例７２	2.5	230	980	無し
例７３	13.4	50	1010	無し
例７４	9.8	135	1140	無し
例７５	2.4	230	1040	無し
例７６	2.1	230	930	無し
例７７	1.2	460	860	無し
例７８	1.1	820	830	無し
例７９	1.1	1520	780	無し
例８０	1.1	2830	720	無し
例８１	1.2	790	990	有り

Key: 1   OH group concentration
2   Fluorine concentration
3   Virtual temperature
4   Presence of reduction defect
5   Example
6   No
7   Yes

Table 14

	157 nm内部透過率 (%／cm)
例66	59. 1
例67	73. 9
例68	78. 6
例69	82. 6
例70	85. 6
例71	94. 0
例72	89. 0
例73	64. 3
例74	69. 5
例75	86. 7
例76	92. 1
例77	95. 7
例78	96. 1
例79	96. 6
例80	96. 8
例81	63. 3

Key: 1   157 nm internal transmittance
       2   Example

Examples 82-85

SiCl$_4$ and SiF$_4$ were hydrolyzed and oxidized in an oxyhydrogen flame at 1800-2000°C by a known direct method to directly synthesize a 250 mmφ transparent quartz glass on a substrate. The transparent quartz glass was drawn to a 200 mmφ rod and kneaded by the horizontal zone melting method (FZ method) to homogenize. Then, it was set in an electric furnace, kept at 1250° for a fixed time, slowly cooled to 800°C at a cooling rate of 1°C/h, and naturally cooled to obtain a synthetic quartz glass.

In the aforementioned manufacturing process, the fluorine concentration and its distribution were controlled by controlling the mixing ratio of SiCl$_4$ and SiF$_4$, in addition, the OH group concentration and its distribution and also the hydrogen molecule concentration were controlled by controlling the flow ratios of oxygen and hydrogen to obtain the synthetic quartz glass samples shown in Examples 82-85 of Tables 15 and 16.

Examples 86-94

SiO$_2$ fine particles, which were obtained by hydrolyzing SiCl$_4$ in an oxyhydrogen flame at 1200-1500°C according to a known soot method, were deposited on a substrate to obtain a

porous quartz glass body of 300 mmϕ x length 800 mm. It was set in an environment controllable electric furnace, and helium gas containing 1 vol % of a fluorine compound was fed into the electric furnace at a reduced pressure of 10 torr or less. Then, it was kept in this environment at normal pressure and room temperature for several hours to simultaneously carry out dehydration and fluorine doping of the porous quartz glass body. Then, it was heated to 1450°C at a reduced pressure of 10 torr or less and kept at this temperature for 10 h to prepare a transparent quartz glass body (105 mmϕ x length 650 mm).

Furthermore, the transparent quartz glass body was heated in an electric furnace having carbon heating elements to 1750°C, which was higher than the softening point, to carry out dead load deformation along the growth axis direction to obtain a columnar block. Then, the temperature of the electric furnace was dropped to 1250°C at the setting up state of the molded block, and a slow cooling at a cooling rate of 1°C/h was conducted, and when the inner temperature of the furnace reached 800°C, the power supply was cut off. The quartz block thus obtained was cut to a thickness of 30 mm and doped with hydrogen by holding in a hydrogen-containing environment at 500°C for 240 h to obtain synthetic glass Examples 82-94 in Tables 14-19 [sic; 15-19].
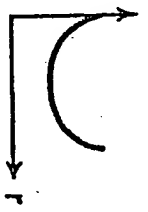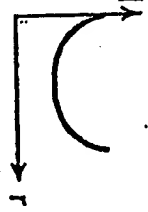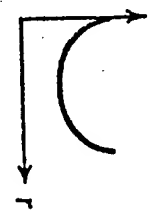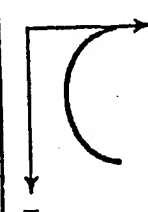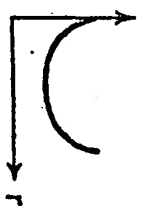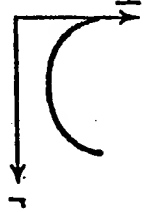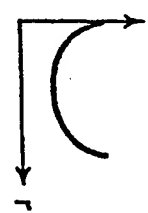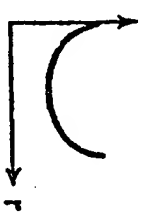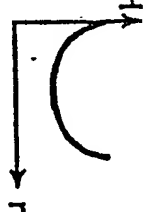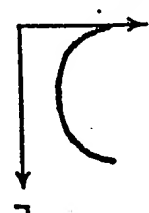
In the aforementioned manufacturing process, the OH group concentration and fluorine concentration in the synthetic quartz glass were controlled by controlling the flow ratios of oxygen and hydrogen gases to the raw material gas or by controlling the concentration of fluorine compound and holding time for the porous quartz glass body in the fluorine compound-containing environment. In addition, the fluctuation widths of the OH group concentration and fluorine concentration in the synthetic quartz glass were controlled by controlling the molding size. Furthermore, the hydrogen molecule concentration in the synthetic quartz glass was controlled by controlling conditions in the heat treatment in the hydrogen-containing environment.

The fluorine concentration and its fluctuation width, the OH group concentration and its fluctuation width, the chlorine concentration, and the hydrogen molecule concentration of the synthetic quartz glass obtained in Examples 82-94 were measured.

Then, the refractive index distribution, L_{650}/S_{248}, and internal transmittance of samples from the synthetic quartz glass of Examples 82-94 were measured to evaluate those samples.

Evaluation results are shown in Tables 15-21. Furthermore, Examples 82-84, Examples 87-91, and Example 94 are application examples of the present invention, and the others are comparative examples.

Table 15

製法	F 濃度 (ppm)			OH 基濃度 (ppm)			塩素濃度 (ppm)			屈折率変動幅
例82 直接法	最大 = 900 最小 = 885 変動幅 = 15 F			最大 = 950 最小 = 935 変動幅 = 15 OH			最大 = 23 最小 = 14 変動幅 = 9 Cl			n 6.6 ppm
例83 直接法	最大 = 895 最小 = 890 変動幅 = 5 F			最大 = 945 最小 = 940 変動幅 = 5 OH			最大 = 23 最小 = 18 変動幅 = 5 Cl			n 2.0 ppm
例84 直接法	最大 = 893 最小 = 891 変動幅 = 2 F			最大 = 943 最小 = 941 変動幅 = 2 OH			最大 = 23 最小 = 20 変動幅 = 3 Cl			n 0.7 ppm

Key: 1   Preparation method
      2   F concentration
      3   OH group concentration
      4   Chlorine concentration
      5   Fluctuation width of refractive index
      6   Example
      7   Direct method
      8   Maximum =
           Minimum =
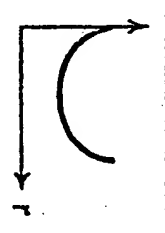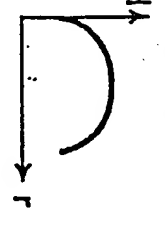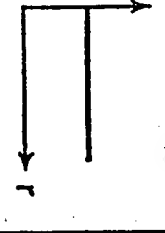   Fluctuation width =

Table 16
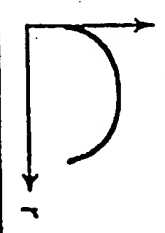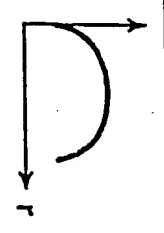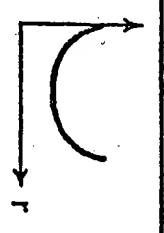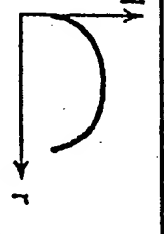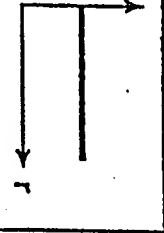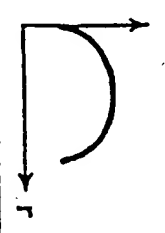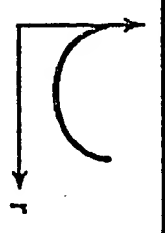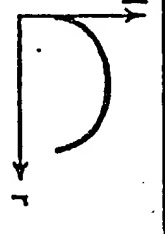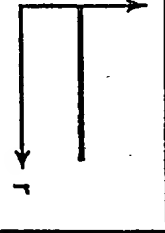
製法	F濃度 (ppm)	OH基濃度 (ppm)	塩素濃度 (ppm)	屈折率変動幅
例85 直接法	最大 = 940 最小 = 910 変動幅 = 30	最大 = 960 最小 = 930 変動幅 = 30	最大 = 21 最小 = 14 変動幅 = 7	14.3 ppm
例86 直接法	最大 = 936 最小 = 914 変動幅 = 22	最大 = 956 最小 = 934 変動幅 = 22	最大 = 68 最小 = 53 変動幅 = 15	9.5 ppm
例87 スート法	最大 = 606 最小 = 583 変動幅 = 23	最大 = 40 最小 = 18 変動幅 = 22	最大 = 10 最小 = 7 変動幅 = 3	6.7 ppm

Key: 1   Preparation method
2   F concentration

3 OH group concentration

4 Chlorine concentration

5 Fluctuation width of refractive index

6 Example

7 Direct method

8 Maximum =

Minimum =

Fluctuation width =

9 Soot method

Table 17

	製法	F濃度 (ppm)	OH基濃度 (ppm)	塩素濃度 (ppm)	屈折率変動幅
例88	スート法	最大 = 598 最小 = 596 変動幅 = 2	最大 = 28 最小 = 26 変動幅 = 2	最大 = 8 最小 = 8 変動幅 = 0	0.6 ppm
例89	スート法	最大 = 617 最小 = 615 変動幅 = 2	最大 = 24 最小 = 23 変動幅 = 1	最大 = 8 最小 = 8 変動幅 = 0	0.7 ppm
例90	スート法	最大 = 639 最小 = 637 変動幅 = 2	最大 = 10.5 最小 = 10.1 変動幅 = 0.4	最大 = 8 最小 = 8 変動幅 = 0	0.8 ppm

Key: 1   Preparation method
     2   F concentration

3   OH group concentration
4   Chlorine concentration
5   Fluctuation width of refractive index
6   Example
7   Soot method
8   Maximum =
        Minimum =
        Fluctuation width =

Table 18

製法 (Preparation method)	F濃度 (ppm)	OH基濃度 (ppm)	塩素濃度 (ppm)	屈折率変動幅
例91 スート法	最大 = 715 最小 = 713 変動幅 = 2	最大 = 5.6 最小 = 5.5 変動幅 = 0.1	最大 = 8 最小 = 8 変動幅 = 0	0.8 ppm
例92 スート法	最大 = 557 最小 = 515 変動幅 = 42	最大 = 75 最小 = 20 変動幅 = 55	最大 = 10 最小 = 6 変動幅 = 4	10.9 ppm
例93 スート法	最大 = 634 最小 = 592 変動幅 = 42	最大 = 59 最小 = 31 変動幅 = 28	最大 = 10 最小 = 6 変動幅 = 4	13.6 ppm

Key: 1   Preparation method

52

2   F concentration
3   OH group concentration
4   Chlorine concentration
5   Fluctuation width of refractive index
6   Example
7   Soot method
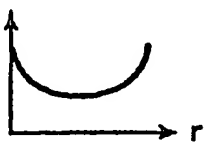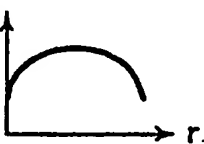8   Maximum =
          Minimum =
          Fluctuation width =

Table 19

	製法	F 濃度 (ppm)	OH 基濃度 (ppm)	塩素濃度 (ppm)	屈折率変動幅
例 94	スート法	最大 = 730 最小 = 728 変動幅 = 2	最大 = 3.7 最小 = 3.6 変動幅 = 0.1	最大 = 8 最小 = 8 変動幅 = 0	0.8 ppm
		F ⌣ →r	OH ⌢ →r	Cl — →r	n ⌢ →r

Key: 1   Preparation method
       2   F concentration
       3   OH group concentration
       4   Chlorine concentration
       5   Fluctuation width of refractive index
       6   Example
       7   Soot method
       8   Maximum =
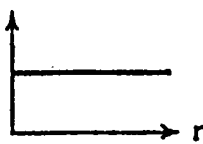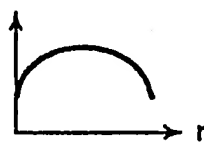   Minimum =
           Fluctuation width =

Table 20

例	水素分子濃度 [分子/cm³]	ΔK$_{214}$ [cm⁻¹]		L$_{650}$/S$_{248}$ [−]	
		最大	最小	最大	最小
例84	3.1×10^{18}	8.8×10^{-3}	8.6×10^{-3}	36.3×10^{-5}	36.0×10^{-5}
例85	3.1×10^{18}	9.1×10^{-3}	8.8×10^{-3}	36.2×10^{-5}	36.1×10^{-5}
例86	3.1×10^{18}	9.1×10^{-3}	8.7×10^{-3}	36.2×10^{-5}	36.1×10^{-5}
例87	3.1×10^{18}	1.6×10^{-2}	1.6×10^{-2}	36.5×10^{-5}	35.9×10^{-5}
例88	1.8×10^{18}	8.8×10^{-3}	8.4×10^{-3}	36.4×10^{-5}	35.9×10^{-5}
例89	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-3}	6.0×10^{-5}	3.5×10^{-5}
例90	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-3}	4.1×10^{-5}	4.0×10^{-5}
例91	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-3}	2.5×10^{-5}	2.4×10^{-5}
例92	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-3}	1.7×10^{-5}	1.7×10^{-5}
例93	1.8×10^{18}	5.9×10^{-3}	5.9×10^{-3}	8.1×10^{-5}	3.7×10^{-5}
例94	1.8×10^{18}	6.2×10^{-3}	6.2×10^{-3}	7.0×10^{-5}	4.8×10^{-5}
例95	1.7×10^{17}	6.1×10^{-3}	6.1×10^{-3}	11.0×10^{-5}	10.9×10^{-5}
例96	1.8×10^{18}	5.9×10^{-3}	5.9×10^{-3}	21.3×10^{-5}	21.2×10^{-5}

Key: 1 Hydrogen molecule concentration

54

[molecules/cm^3]
2   Maximum
3   Minimum
4   Example

Table 21

	157nm 内部透過率（%/cm)	
	最大	最小
例 84	<0.1	<0.1
例 85	<0.1	<0.1
例 86	<0.1	<0.1
例 87	<0.1	<0.1
例 88	<0.1	<0.1
例 89	58.0	39.2
例 90	49.7	48.0
例 91	52.6	51.6
例 92	69.2	68.5
例 93	78.3	78.1
例 94	55.7	23.9
例 95	45.5	29.6
例 96	83.8	83.3

Key: 1   157 nm Internal transmittance
      2   Maximum
      3   Minimum
      4   Example

Industrial application potential

A synthetic quartz glass, which is excellent in ultraviolet ray transmittance and diminishes the reduction of transmittance due to the generation of E' centers by irradiation of high energy beams from a light source such as excimer or radiation and also reduces fluorescence illumination to improve ultraviolet ray resistance, is obtained by the present invention.

In addition, a synthetic quartz glass which is excellent in vacuum ultraviolet transmittance can be obtained by the present invention. Especially, a synthetic quartz glass having high

transmittance even in the vacuum ultraviolet region at a wavelength of 200 nm or less can be obtained.

Furthermore, a synthetic quartz glass which is excellent in homogeneity and ultraviolet ray resistance can be obtained.

Thus, the synthetic quartz glass of the present invention is extremely suitable as a constituent part of optical systems which are used by irradiation of light rays from the ultraviolet region to the vacuum ultraviolet region.

Furthermore, a synthetic quartz glass, which is excellent in the aforementioned ultraviolet ray resistance, vacuum ultraviolet ray transmittance, or homogeneity, can be easily produced by the present invention.

Claims

1. A synthetic quartz glass for optical use which is used by irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, characterized in that the quartz glass contains fluorine and has a ratio of the intensity of the scattering peak at 2250 cm^{-1} (I_{2250}) to that of the scattering peak at 800 cm^{-1} (I_{800}), that is I_{2250}/I_{800}, in a laser Raman spectrum of 1×10^{-4} or less and an absorption coefficient of light having a wavelength of 245 nm of 2×10^{-3} cm^{-1} or less.

2. The synthetic quartz glass described in Claim 1, wherein the fluorine concentration is 100 ppm or higher.

3. The synthetic quartz glass described in Claim 1, wherein the OH group concentration is 100 ppm or less.

4. The synthetic quartz glass described in any one of Claims 1-3, wherein the chlorine concentration is 100 ppm or less.

5. The synthetic quartz glass described in any one of Claims 1-4, wherein the ratio of the intensity of the scattering peak at 495 cm^{-1} (I_{495}) to that of the scattering peak at 440 cm^{-1} (I_{440}) in a laser Raman spectrum and also the ratio of the intensity of the scattering peak at 606 cm^{-1} (I_{606}) to the I_{440}, that is I_{495}/I_{440} and I_{606}/I_{440}, are 0.585 or less and 0.136 or less, respectively.

6. The synthetic quartz glass described in any one of Claims 1-5, wherein the OH group concentration is 50 ppm or less.

7. The synthetic quartz glass described in any one of Claims 1-5, wherein the OH group concentration is 10 ppm or less.

8. The synthetic quartz glass described in any one of Claims 1-5, which is a synthetic quartz glass to be used in a region at a wavelength of 160 nm and less, wherein the OH group concentration is 5 ppm or less.

9. The synthetic quartz glass described in any one of Claims 1-8, wherein the virtual temperature is 1100°C or less.

10. The synthetic quartz glass described in Claim 8 or 9, wherein the internal transmittance at a wavelength of 157 nm is 80%/cm or higher.

11. A synthetic quartz glass for optical use which is used through irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, characterized in that the synthetic quartz glass contains OH groups and fluorine and has a fluctuation width of the OH group concentration of 15 ppm or less, a fluctuation width of the fluorine concentration of 15 ppm or less in the light application area, and also a chlorine concentration of 25 ppm or less.

12. A synthetic quartz glass for optical use which is used through irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, characterized in that the synthetic quartz glass contains OH groups and fluorine, and the OH groups and the fluorine are distributed in the light application area in such a manner to mutually negate each others concentration distribution so that the synthetic quartz glass has a fluctuation width of the OH group concentration of 25 ppm or less, a fluctuation width of the fluorine concentration of 25 ppm or less, and a chlorine concentration of 25 ppm or less.

13. The synthetic quartz glass described in Claim 11 or 12, wherein the sum of the fluctuation width of the fluorine concentration and the fluctuation width of the OH group concentration is 5 ppm or less.

14. The synthetic quartz glass described in any one of Claims 11-13, wherein the fluctuation width of the refractive index in a plane perpendicular to an incident light (Δn) is 20×10^{-6} or less.

15. The synthetic quartz glass described in any one of Claims 11-13, wherein the fluctuation width of the refractive index in a plane perpendicular to an incident light (Δn) is 5×10^{-6} or less.

16. A method for the manufacture of a synthetic quartz glass for optical use which is used through irradiation of rays of light from the ultraviolet region to the vacuum ultraviolet region, characterized by comprising

(a) a process of depositing and growing quartz glass fine particles, obtained by flame hydrolysis of a quartz glass forming raw material, on a substrate to form a porous quartz glass body,

(b) a process of keeping the porous quartz glass body in a fluorine-containing environment to obtain a fluorine-containing porous quartz glass, and

(c) a process of vitrifying to transparency the fluorine-containing porous quartz glass body by heating to transparency-forming, vitrification temperature to obtain a transparent quartz glass body.

17. The method for the manufacture of a synthetic quartz glass described in Claim 16,

wherein in process (b), the fluorine-containing environment is prepared by maintaining the environment at a temperature of less than 600°C and at a reduced pressure and then feeding a fluorine-containing gas into it.

18. The method for the manufacture of a synthetic quartz glass described in Claim 16 or 17, wherein a process (e) described below is inserted between process (b) and the process (c);
(e) [being] a process of reducing the pressure of the environment and allowing a fluorine-containing porous quartz glass body to stand in the environment under a reduced pressure for a prescribed time.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/05995

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁷ C03C3/06, C03B8/04, C03B20/00
G03F1/16, G02B1/00, H01L21/027

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁷ C03C3/06, C03B8/04, C03B20/00
C03B37/00-37/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho   1922-1996   Toroku Jitsuyo Shinan Koho   1994-2000
Kokai Jitsuyo Shinan Koho   1971-2000   Jitsuyo Shinan Toroku Koho   1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI/L
JICST(JOIS)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 10-067526, A (NIKON CORPORATION), 10 March, 1998 (10.03.98), Claims 1-2; Par. Nos. [0008]-[0009], [0012]-[0014], [0017], [0019], [0022] & EP, 835848, A2 & JP, 10-067521, A & JP, 10-218636, A & US, 5958809, A	1-2,4-5,9-10 3,6-8,11-15
X Y	EP, 691312, A1 (NIKON CORPORATION), 10 January, 1996 (10.01.96), Claim 1, 13-14; page 2, lines 5-12, (Field of the Invention); page 3, line 43 to page 4, line 4; page 4, lines 13-20; page 5, lines 5-20 & US, 5679125, A & EP, 691312, B1 & DE, 69501523, E & JP, 08-075901, A Claim 1, 14-15; Par. Nos. [0001], [0010]-[0012], [0014], [0020]-[0022]	16,18 3,6-8,11-15,17

☒ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*   Special categories of cited documents:
"A"   document defining the general state of the art which is not considered to be of particular relevance
"E"   earlier document but published on or after the international filing date
"L"   document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"   document referring to an oral disclosure, use, exhibition or other means
"P"   document published prior to the international filing date but later than the priority date claimed

"T"   later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"   document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"   document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"   document member of the same patent family

Date of the actual completion of the international search 20 January, 2000 (20.01.00)	Date of mailing of the international search report 01 February, 2000 (01.02.00)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/05995

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 5336941, A (Asahi Glass Co., Ltd.), 19 July, 1994 (19.07.94), page 2, column 2, lines 27-47; page 7, column 12, lines 15-24 line 24 & JP 2861512, B2 & JP. 05-024856, A Claims 1-2; Par. Nos. [0006]-[0007]	11-15
Y	JP, 03-008743, A (Shin-Etsu Chemical Co., Ltd.), 16 January, 1991 (16.01.91), Claim 2; page 3, lower left column, lines 8-14; page 3, lower right column, line 15 to page 4, upper left column, line 1; page 4, upper right column, line 20 to lower left column, line 6 (Family: none)	17
EX	JP, 11-305419, A (NIKON CORPORATION), 05 November, 1999 (05.11.99), Claims 1, 2; Par. Nos. [0063]-[0064], [0067], [0079], [0082]-[0083] (Family: none)	1-2,4-5,9-10, 16,18